United States Environmental Protection Agency Office of Air Quality Planning and Standards Research Triangle Park, NC 27711 EPA-454/R-98-002 April 1998

Air

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Guideline On Ozone Monitoring Site Selection



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EXECUTIVE SUMMARY

OVERVIEW

This report provides background information for State and local agencies responsible for designing and implementing an ozone monitoring program. The purpose of this report is to update a 1978 U.S. Environmental Protection Agency (EPA) report entitled: "Site Selection for the Monitoring of Photochemical Air Pollutants" (EPA, 1978). This updated report, "Guideline on Ozone Monitoring Site Selection," is motivated by the need to help air quality agencies and others incorporate 8-hour monitoring into their ozone monitoring program. Since the 1970s, ozone monitoring programs have been designed to address the 1-hour ozone National Ambient Air Quality Standard (NAAQS); however, on July 18, 1997, the U.S. EPA promulgated an 8-hour ozone NAAQS. This report assists those agencies considering how to design and implement ozone monitoring networks, particularly in light of the need to collect 8-hour ozone concentration data.

The report covers basic issues essential to understanding monitor siting considerations, including the following:

- The physics and chemistry of ozone formation: The report includes a description of ozone chemistry, the relationship between precursor and ozone concentrations, and meteorological conditions that are most conducive to ozone formation.
- Spatial distribution of ozone concentrations: Distributions of ozone concentrations
 across a metropolitan areas are examined and related to ozone chemistry and meteorology.
 Also included is a comparison of the spatial distribution of 1-hour and 8-hour ozone
 concentrations.
- *Monitoring objectives and network design:* Purposes of ozone monitoring are described, as well as the types and number of monitoring sites that are recommended.
- *Macroscale considerations for monitor placement:* Techniques are recommended to identify general locations for the required monitor types for a metropolitan area.
- *Microscale considerations for monitor placement:* Techniques are recommended for finding specific locations for ozone monitors.

Appendices include background information on ozone formation, and references to supplemental materials that can assist those involved with siting efforts.

REVIEW OF KEY FINDINGS AND RECOMMENDATIONS

In this report, improved knowledge and understanding of ozone photochemistry is used to reach a series of conclusions and recommendations regarding ozone monitoring networks. In particular:

Ozone Formation (Section 2.)

Section 2. includes a description of the physics and chemistry of ozone formation (a supplement to this section is included as Appendix A). The following key principles are illustrated:

- Ozone is a secondary pollutant formed in the atmosphere by reactions between oxides of nitrogen (NO_x) and volatile organic compounds (VOC).
- The relationship between the precursor concentrations and ozone formation must be considered when developing control strategies. Ozone formation in some geographic areas may be limited by the supply of NO_x, while in other areas ozone formation may be limited by the supply of VOC.
- Ozone formation is most conducive during warm, dry, and cloudless days with low wind speeds; these conditions most often occur during high-pressure systems. Consequently, ozone monitoring should take place during the warmer periods of the year.

Spatial Distribution of Ozone Concentrations (Section 3.)

Using examples from the San Francisco Bay Area and the northeastern United States, Section 3. includes a discussion of the urban and regional distribution of ozone concentrations. The following key principles are discussed:

- Generally, the highest ozone concentrations in a metropolitan area are found downwind of the urban fringe.
- The locations of the peak concentrations of a 0.12 ppm 1-hour and a 0.08 ppm 8-hour threshold are similar; however, downwind sites may be more prone to 8-hour exceedances relative to 1-hour exceedances.
- Subtle differences exist between the 1-hour and 8-hour forms. For example, downwind sites which receive transported, dispersed ozone plumes and have low NO concentrations available to titrate ozone, will have flatter diurnal concentration profiles that are more prone to 0.08 ppm 8-hour exceedances, relative to 0.12 ppm 1-hour exceedances. Also, the ratio of the 8-hour running average ozone concentration and the 1-hour daily

maximum ozone concentration generally increases from urban centers, suggesting that rural sites may be more prone to 8-hour exceedances than to 1-hour exceedances.

Monitoring Objectives and Network Design (Section 4.)

This section introduces the basis for establishing a monitoring network. Key points include:

- Ozone monitoring objectives can be several-fold, including determining regulatory compliance, developing control strategies, and collecting data for health studies and air quality studies.
- A minimum of two ozone monitors are required for urbanized areas with populations greater than 200,000. If a nonattainment area is designated as serious, severe, or extreme for the 1-hour ozone standard, then up to five monitors are required as a part of the Photochemical Assessment Monitoring Stations (PAMS) program.
- · In general, 8-hour ozone monitoring seasons are slightly smaller than those established for the 1-hour standard.

Macroscale Considerations in Monitor Siting (Section 5.)

This section focuses on identifying general locations within a metropolitan area to site ozone monitors. Recommendations include:

- Upwind monitors should be located along the trajectory of the morning prevailing wind direction (PWD), and the downwind monitor should be located along the trajectory of the afternoon PWD. Upwind monitoring will help establish background ozone and ozone precursor concentrations (if PAMS) entering the geographic area, and downwind monitors will help evaluate the peak ozone concentrations experienced within the geographic area.
- PWDs should be determined from wind rose plots of days where high concentrations of ozone are measured, or days conducive to ozone formation. Specific meteorological criteria based upon temperature, wind speed, and relative humidity can help identify days conducive to ozone formation. These factors vary depending upon local conditions, and the section describes how these criteria can be applied to different parts of the country.
- For areas where ozone episodes are dominated by stagnation conditions and for which a dominant PWD cannot be discerned, ozone monitors should be located along the major axes of the emission sources within 10 miles of the urban fringe (i.e., no further than 10 miles beyond the outermost portion of the urban fringe).
- For re-evaluating a network pursuant to the 8-hour running average concentration, the potential for changes in the spatial distribution of exceedances needs to be evaluated.

Generally, 1-hour and 8-hour ozone concentrations are well correlated spatially. However, downwind sites are more prone to 8-hour exceedances than to 1-hour exceedances, and the total geographic area monitored may need to expand to measure 8-hour ozone values.

Microscale Considerations in Monitor Siting (Section 6.)

This section provides guidance on determining specific monitor locations after the general locations are determined (Appendix B provides references to supplemental materials useful in developing a monitoring program). Key recommendations from this section include:

- · Probe inlets should be placed 3 to 15 meters above ground level.
- Samplers should be separated from any obstruction such as a building by at least twice the height that the obstruction protrudes above the sampling inlet.
- Monitors should be placed an adequate distance from roadways. The more traffic on a road, the greater the recommended distance between the roadway and the monitor location. For example, for roads with 10,000 or less vehicles per day, monitors should be at least 10 meters away from the roadway; roads with 110,000 vehicles per day or more should have monitors sited at least 250 meters away from the roadway.
- Inlet probes should be placed at least 20 meters from the drip line of trees to minimize interferences. Large trees or stands of trees should be treated as large obstructions, e.g., as buildings, however, the probe must be not be located less than 10 meters from the drip line of such trees treated as obstructions.
- · "Saturation monitoring" can also be used to site monitors. Saturation monitoring involves the deployment of numerous portable monitors on a short-term basis to quickly develop a better understanding of how ozone concentrations vary across a geographic area.

Summary (Section 7.)

The recommendations provide real world examples to illustrate how geographic areas should conduct their monitoring activities, answer common questions, and provide practical "rules of thumb" for those engaged in monitoring network design. These are organized in response to commonly asked questions such as:

- · How many monitors are enough to provide adequate coverage for a particular region?
- · How should monitors be sited to properly account for wind direction?
- · How should monitors be sited to avoid problems in the immediate vicinity of the monitor (e.g., from roads, trees, buildings)?

- · Are existing 1-hour monitoring sites still useful for 8-hour monitoring, or should they be moved? In particular, does an 8-hour standard mean that the geographic area monitored needs to be enlarged, and if so, by how much?
- · How can monitor sites be evaluated to determine if they are located in appropriate downwind locations to identify peak ozone concentrations?
- Should 8-hour ozone monitoring be conducted during the same time of the year as 1-hour ozone monitoring?
- · How should monitor siting differ depending upon whether an area is an isolated urban area, is part of an urban corridor which includes numerous metropolitan areas, or is an urban area with multiple prevailing wind directions?

1. INTRODUCTION

This report provides background information for those responsible for designing and implementing an ozone monitoring program. Its purpose is to update the 1978 U.S. Environmental Protection Agency (EPA) report entitled: "Site Selection for the Monitoring of Photochemical Air Pollutants" (EPA, 1978). This updated report, "Guideline on Ozone Monitoring Site Selection," is motivated by the need to help air quality agencies and others incorporate 8-hour monitoring into their ozone monitoring program. Since the 1970s, ozone monitoring programs have been designed to address the 1-hour ozone National Ambient Air Quality Standard (NAAQS); however, on July 18, 1998, the U.S. EPA promulgated an 8-hour ozone NAAQS. This report assists those agencies considering how to design and implement ozone monitoring in light of the need to collect 8-hour ozone concentration data. In addition, knowledge of ozone photochemistry has improved in recent years and it is timely to revisit monitoring network design issues in light of new scientific knowledge.

One of the first steps in recognizing or diagnosing an air pollution problem is the development of an adequate monitoring network to quantify pollution concentrations. Specifically, there are five major objectives to air monitoring:

- Determine the highest concentrations expected to occur in the area covered by the network.
- Determine representative concentrations in areas of high population density.
- Determine the impact of specific sources or source categories on ambient pollution concentrations.
- · Determine general background concentrations.
- Determine the extent of air pollution transport into and out of an area.

Numerous decisions need to be made in designing a monitoring network, including:

- · How many monitors are needed?
- · What pollutants need to be measured?
- · Where should the monitors be placed?
- During which part of the year is monitoring needed?

In the years since the EPA produced its 1978 guidance for designing monitoring networks for photochemical pollutants (EPA, 1978), there have been significant advances in the understanding of the chemistry of photochemical air pollution. Also, moving from a 1-hour daily maximum ozone concentration NAAQS to an 8-hour running average concentration NAAQS means different geographic areas may be affected. Such differences suggest changes to traditional monitoring networks.

The principal focus of this report is ozone, but a few remarks are made regarding NO monitoring as it relates to ozone formation. EPA's 1978 document addressed monitoring placement criteria for nonmethane hydrocarbons (NMHC), nitrogen dioxide (NO₂), nitric oxide (NO), and ozone (or oxidants, on which the standard was then based). There is no longer a NMHC standard, and there are presently no areas in violation of the current NO₂ NAAQS. Therefore, these pollutants are not addressed. It is worth noting that since 1991, hydrocarbons that are considered precursors to ozone are now required to be measured in selected ozone nonattainment areas at sites called Photochemical Assessment Monitoring Stations (PAMS). A separate document was prepared by the EPA to address the selection of PAMS sites (EPA, 1994).

This report is organized into seven main sections:

- 1. *Introduction* (this discussion).
- 2. *Important Characteristics of Ozone Formation:* Provides the reader with a general explanation of ozone formation chemistry, the importance of ozone precursor emissions, and meteorological conditions conducive to ozone formation.
- 3. Spatial Distribution of Ozone Concentrations: Describes the spatial nature of ozone concentrations and how these differ on a 1-hour and 8-hour basis. The section provides example ozone concentration situations in the western and northeastern United States.
- 4. *Monitoring Objectives and Network Design:* Discusses under what conditions to monitor in neighborhoods versus urban or regional settings, monitoring for regulatory compliance versus control strategy development, the number of required monitor sites, and the seasons during which monitoring should occur.
- 5. *Macroscale Considerations in Monitor Siting:* Provides guidance for determining the general location of monitors in a metropolitan area.
- 6. *Microscale Considerations for Monitor Siting:* Provides guidance for the specific placement of monitors, once the general location has been identified.
- 7. Recommendations: Summarizes the key recommendations included in the report.

The report also includes references and two appendices: Appendix A, which contains information on ozone formation, and Appendix B, which contains citations for additional information resources of interest to those involved with monitor siting.

2. IMPORTANT CHARACTERISTICS OF OZONE FORMATION

Ozone is not generally emitted by sources, but instead is formed in the atmosphere by a series of complex chemical reactions between oxides of nitrogen and organic compounds. The process of ozone formation is complex. However, a basic understanding of this chemistry is necessary for predicting the spatial distribution of the ozone concentration within a metropolitan or regional area, and for developing an ozone monitoring network. This section provides background information on ozone formation and includes brief discussions on the following (More detail on the photochemical reactions contributing to ozone formation can be found in Appendix A.):

- · Ozone formation chemistry in the troposphere
- · Sources and spatial distribution of ozone precursor emissions
- Meteorological conditions conducive to ozone formation.

Figure 2-1 shows a general schematic diagram of ozone formation in the atmosphere. This section describes these processes and their interactions. These principles are illustrated further in Section 3., which describes the spatial and temporal distribution of ozone concentrations.

2.1 OZONE FORMATION CHEMISTRY

2.1.1 Basic Principles

The basis for ozone formation is the photolysis of nitrogen dioxide (NO₂), by the following reactions (Seinfeld, 1986):

$$NO_2 + h \cap \xrightarrow{k_1} NO + O$$
 (2-1)

$$O + O_2 + M \xrightarrow{k_2} O_3 + M \tag{2-2}$$

where $h \cap$ represents photochemical energy from ultraviolet radiation (or a photon), k represents a rate constant for the reaction of NO_2 and $h \cap$ and M represents N_2 or O_2 or another molecule that absorbs the reaction's excess vibrational energy. Once formed, ozone is rapidly dissociated by reaction with NO_2 as follows:

$$O_3 + NO \xrightarrow{k_3} NO_2 + O_2 \tag{2-3}$$

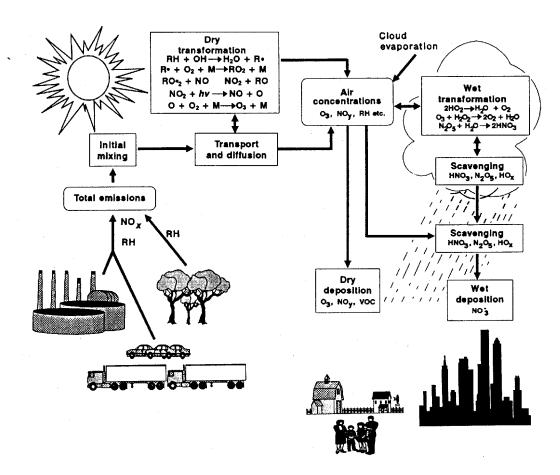


Figure 2-1. Schematic diagram of photochemical air pollution from emission to deposition (NAS, 1991)

The NO_2 molecule is regenerated, and in the absence of other species a steady state is achieved through reactions (2-1) through (2-3) in which the ozone concentration can be estimated by the following relationship:

$$\left[O_{3}\right] = \frac{k_{1}\left[NO_{2}\right]}{k_{3}\left[NO\right]} \tag{2-4}$$

In the natural troposphere, these reactions normally result in a background ozone concentration of 15 to 45 parts per billion (ppb) (Altshuller and Lefohn, 1996).

Emissions of volatile organic compounds (VOC) are key contributors to ozone concentrations above normal background values. Most combustion and biogenic emissions of oxides of nitrogen are emitted in the form of NO, although some of the NO in the combustion gases are oxidized to NO₂. In the atmosphere, VOC facilitate the oxidation of NO to NO₂, thus allowing for continued ozone production while reducing the destruction of ozone by NO.

VOC sources are both anthropogenic and natural in origin. Anthropogenic sources include automobiles, chemical production, and other industrial activities. Many species of vegetation including trees and plants naturally emit VOC. In the natural troposphere, there is a sufficient amount of natural (or biogenic) VOC to oxidize some of the NO to NO₂, which results in the background ozone concentration discussed above. When additional VOC is added to the atmosphere, a greater proportion of the NO is oxidized to NO₂, resulting in greater ozone formation. Additionally, anthropogenic sources of NO, including sources such as automobiles and electric utility plants, result in greater levels of NO₂ in the atmosphere, which is then available for photolysis to NO and O and, ultimately, NO and ozone.

Using the chemical principles elucidated above, EPA's Empirical Kinetic Modeling Approach (EKMA) can be used to depict a simplistic but concise diagram for predicting the effects of changes in VOC or NO_x concentrations. **Figure 2-2** shows a typical set of EKMA ozone isopleths. The ozone isopleths depend on the VOC/ NO_x ratio. For low VOC/ NO_x ratios, the system is VOC limited (i.e., reductions in VOC emissions will reduce the ozone concentrations). Conversely, for high VOC/ NO_x ratios, the system is NO_x limited (i.e., reductions in NO_x emissions will reduce ozone concentrations). The NO_x -limited region is typical of locations downwind of urban and suburban areas, while the VOC-limited region is typical of highly polluted urban areas.

2.1.2 Atmospheric Sinks for Ozone

Once in the atmosphere, ozone can be removed by wet and/or dry deposition. Ozone in contact with the surface can be deposited or adsorbed onto vegetation such as trees and other plants. Also, ozone can be scavenged by precipitation, and can be transformed in the aqueous phase by reaction with other atmospheric constituents such as hydrogen peroxide.

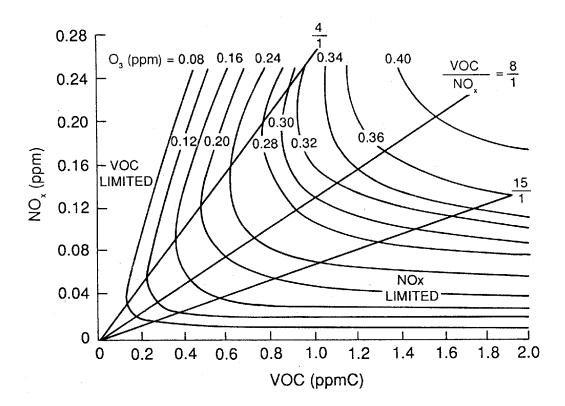


Figure 2-2. Typical ozone isopleths used in the EPA's Empirical Kinetic Modeling Approach (EKMA). The NO_x-limited region is typical of locations downwind of urban and suburban areas, whereas the VOC-limited region is typical of highly polluted urban areas (NAS, 191).

2.2 OZONE PRECURSOR EMISSIONS

2.2.1 Sources of Ozone Precursor Emissions

Table 2-1 summarizes the total anthropogenic emissions of VOC and NO_x in the United States for 1994. The dominant activity for producing NO_x is combustion processes, including industrial and electrical generation processes, and mobile sources such as automobiles. Mobile sources also account for a large portion of VOC emissions. Other industries that process organic materials, such as the chemical industry or others that use solvents, also account for a large portion of the VOC emissions. Although not included in **Table 2-1**, the EPA also estimates the annual biogenic emissions. In 1990, for example, estimated VOC biogenic emissions were 27,000 short tons, which is higher than the anthropogenic emissions. Biogenic VOC emissions include the highly reactive compound isoprene. However, it must be noted that a large proportion of the biogenic VOC emissions are in forested and vegetative areas, where these emissions may not impact urban ozone formation. In contrast to biogenic VOC, which is large relative to anthropogenic emissions, biogenic NO_x emissions (2000 short tons) are much smaller.

2.2.2 Spatial Distribution of Emissions

Anthropogenic VOC and NO_x emissions are generally concentrated around urban areas, due to the nature of the emission sources (e.g., mobile sources [cars, trucks, buses], area sources [including non-road mobile sources], and industry being located in the populated areas of the country). The resulting spatial emission patterns reflect this urban-centered orientation. For example, **Figures 2-3** and **2-4** show the VOC and NO_x emissions (both anthropogenic and biogenic) for 1990 in the northeastern United States. The highest emission densities are near the urban centers of Boston, New York City, Philadelphia, and Baltimore. The emission densities drop rapidly expanding outwards from the urban centers. As will be discussed in more detail later, ozone formation is generally highest downwind of urban centers as a result of the photochemical reaction of ozone precursor emissions in these areas.

2.3 METEOROLOGICAL CONDITIONS CONDUCIVE TO OZONE FORMATION

The chemistry of ozone formation is complex and dependent on numerous variables. Similarly, there are a variety of meteorological variables that influence ozone formation. Although changes in daily emissions can affect daily ozone concentrations, it is the daily variation in meteorological parameters that best explain the daily variations of ozone concentrations. The meteorological conditions which are conducive to ozone formation include:

Days when solar radiation is high: Solar radiation is an important factor because of ozone formation reactions (see Equation 2-1). Solar radiation is highest during cloudless, summer days.

Table 2-1. Summary of VOC and $\rm NO_x$ emissions in the United States during 1994 (U.S. EPA, 1996).

Source Type	NO _x Emissions		VOC Emissions	
,	Emissions (thousand short tons)	Percentage of Total	Emissions (thousand short tons)	Percentage of Total
Fuel Combustion, Electric Utility	7795	33.0	36	0.2
On-Road Vehicles	7580	31.9	6295	27.2
Fuel Combustion, Industrial	3206	13.6	135	0.6
Non-Road Sources	3095	13.1	2255	9.7
Fuel Combustion, Other	727	3.1	715	3.1
Miscellaneous	374	1.6	685	3.0
Other Industrial Processes	328	1.4	411	1.8
Chemical & Allied Product Manufacturing	291	1.2	1577	6.8
Petroleum & Related Industries	95	0.4	630	2.7
Waste Disposal & Recycling	85	0.4	2273	9.8
Metals Processing	84	0.4	77	0.3
Solvent Utilization	3	0.01	6313	27.2
Storage & Transport	3	0.01	1773	7.7

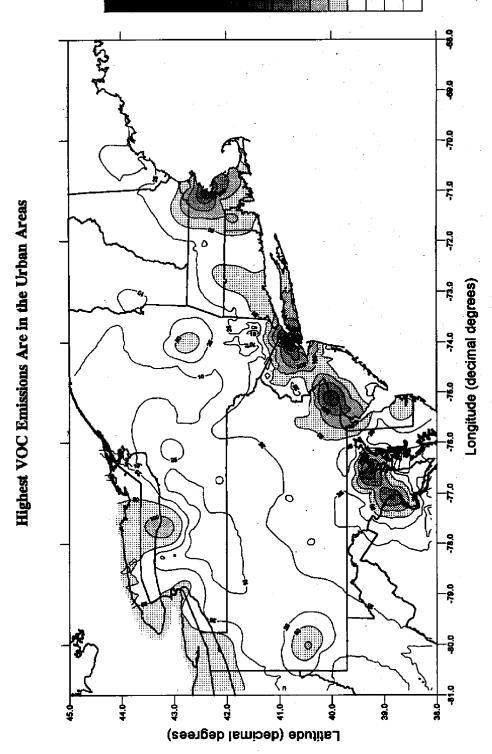
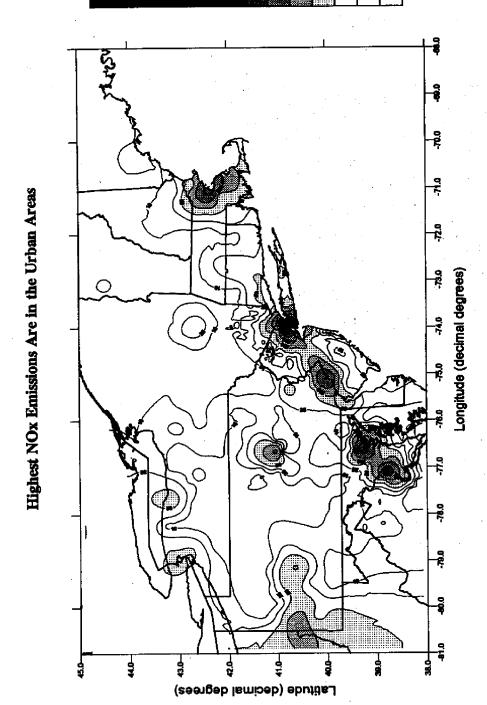


Figure 2-3. Spatial distribution of the anthropogenic VOC emissions (tons per year) in the OTR during 1990. Emissions data are from the 1990 EPA Interim Inventory (EPA, 1996). Emissions are on a countywide basis and assigned to the county centroid.



1200 1200 1000

8

Figure 2-4. Spatial distribution of the anthropogenic NOx emissions (tons per year) in the OTR during 1990. Emissions data are from the 1990 EPA Interim Inventory (EPA, 1992). Emissions are on a countywide basis and assigned to the county centroid.

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- Days with low wind speed: Low wind speeds lead to poorer dispersion and generally result in increased concentration of ozone and ozone precursors within a smaller area. However, areas affected by long-range transport can experience high ozone concentrations during periods of moderate wind speeds.
- Days when mixing heights are low: Strong temperature inversions can cause low mixing heights to occur, which generally lead to increased concentrations of ozone and ozone precursors in a shallow vertical layer.
- Days with low relative humidity: Days with high relative humidity or precipitation are likely to be
 associated with cloudy skies or hazy conditions, which reduce temperatures and solar radiation,
 resulting in decreased ozone concentrations.

The presence of ozone-conducive meteorological conditions can be indicated by the synoptic-scale meteorology (i.e., meteorological conditions over a broad regional area). In particular, ozone concentrations generally accumulate during periods with slow-moving, high-pressure weather systems (NAS, 1991) for the following reasons:

- High-pressure systems are characterized by widespread sinking of air through most of the troposphere, which warms the subsiding air. This tends to make the troposphere more stable and less conducive to mixing, which would disperse ozone and ozone precursor emissions. Temperature normally decreases with altitude in the troposphere, which allows warm air parcels to rise from the surface and mix through the upper troposphere. However, the subsidence of air creates a temperature inversion, which effectively results in a "warm air lid" placed on top of cooler air. The cooler air near the surface fails to mix with the warmer layer above, and there are higher concentrations of ozone and ozone precursors near the surface.
- The light winds associated with high-pressure systems allow for ozone and ozone precursors to accumulate near the emission sources.
- The clear skies associated with high-pressure systems result in increased solar radiation at the surface, which is favorable for photochemical processes.

Ozone-conducive meteorological conditions normally occur during the summertime in most of the United States, except in the southern or "sunbelt" areas where ozone is not restricted to the summer season. Consequently, ozone monitoring is not necessary during the entire year in most areas. Determining the precise monitoring requirement for the ozone season in each metropolitan area of the United States is beyond this report. However, the period during which ozone monitoring is likely to be needed for regulatory compliance in each area of the country is discussed in Section 4.

SPATIAL DISTRIBUTION OF OZONE CONCENTRATIONS

When designing a monitoring network for measuring ozone, it is important to understand the spatial distribution of ozone in the monitoring area. However, the complex process of ozone formation can lead to complex distributions of ozone within a metropolitan area. Several ozone formation process influence this spatial distribution including:

- *Proximity to fresh combustion emissions*: NO _x from fresh combustion emissions is normally in the form of NO, which destroys ozone by chemical reaction (sometimes referred to as NO titration). This results in low ozone concentrations relatively near combustion sources.
- *Distance from primary emission sources*: The process of ozone formation in the atmosphere takes several hours. The maximum concentration normally forms several miles downwind of the primary emission sources because the conversion of precursors requires several hours.
- *Distance and wind speeds through the city*: The direction and speed of winds through the maximum emission area will determine where the ozone and ozone precursors are transported.

Furthermore, 1-hour and 8-hour ozone concentration averaging times have different spatial implications. For example, high 8-hour ozone concentration can be observed over a broader geographic area than high 1-hour ozone concentrations. To illustrate the differences between 1-hour and 8-hour spatial concentration patterns, the next two sections provide examples using observed ozone data from the San Francisco Bay Area (in California) and the northeastern United States. Much of the data and plots for these examples are based on an analysis by Reiss et al., 1995. All of the data portrayed in this report as representing exceedances of the 1-hour and 8-hour thresholds were based on the following "rules of thumb": ozone concentrations equal to or greater than 0.085 ppm over an 8-hour period were an exceedance of the 0.08 ppm 8-hour threshold; all concentrations equal to or greater than 0.125 ppm over a 1-hour period were an exceedance of the 0.12 ppm 1-hour threshold.

3.1 EXAMPLE 1-HOUR AND 8-HOUR OZONE PATTERNS

3.1.1 San Francisco Bay Area

The San Francisco Bay Area has a dense monitoring network encompassing upwind, source and receptor areas. Thus, it can be used to provide a good example of the spatial distribution of ozone within and downwind of a major metropolitan area. The largest urban centers are the cities of San Francisco, Oakland, and San Jose. Generally, the city of San Francisco, the areas south of the city (the San Jose area), and the areas east of the San Francisco Bay are urbanized. Most of the ozone precursor emissions are associated with the urban areas and the industrialized eastern shoreline of the San Francisco Bay and Sacramento River Delta. The areas north of San Francisco (Marin, Sonoma, and Napa counties) are relatively rural and produce fewer ozone precursor emissions. **Figure 3-1** depicts major cities in the San Francisco Bay Area. The meteorology of the region is dominated by costal westerly winds and water-to-land airflows. Therefore, much of the daytime emissions in the urbanized portions of the San Francisco Bay Area are transported to the east and south.

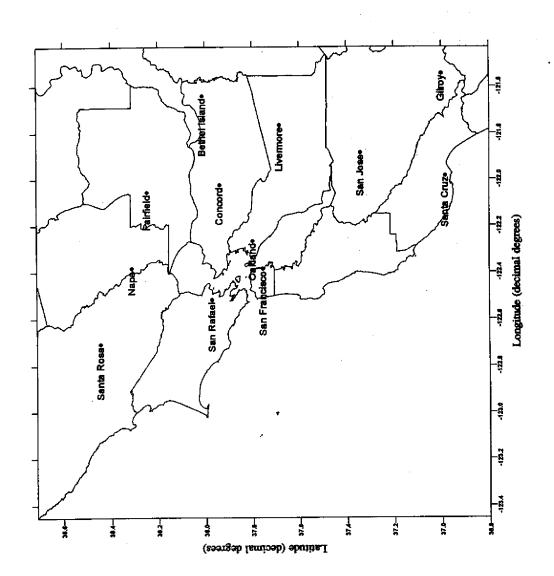


Figure 3-1. Selected cities in the San Francisco Bay Area and downwind regions.

Selected monitoring sites that were active between 1992 and 1995 in the San Francisco Bay Area and downwind areas are shown in Figure 3-2. Table 3-1 lists the sites (city and county) corresponding to the numbers in Figure 3-2. Figures 3-3a and 3-3b, and 3-4a and 3-4b, show the number of exceedances for 1991-1995 of a 0.12 ppm 1-hour threshold, and a 0.08 ppm 8-hour threshold. Figures 3-3a and 3-4a show contours using the number of exceedances to mark each contour interval; Figures 3-3b and 3-4b show the number of exceedances at specific monitors. The figures show information for the San Francisco region and nearby downwind areas. For both the 1-hour and 8-hour thresholds, most of the exceedances are in the eastern and southern portions. There are no exceedances in the city of San Francisco, and there are very few exceedances in the counties north of the city. Three important factors contribute to the clean air in San Francisco: (1) the upwind region is the Pacific Ocean, and thus the air blowing into the San Francisco area is clean to begin with; (2) San Francisco's automobile and truck traffic contributes NO emissions that can titrate ozone; and, (3) except for the area immediately south of San Francisco, nearby areas produce relatively few emissions, so there are fewer emissions that contribute to ozone formation in the immediate vicinity of the city (counties north of San Francisco are largely rural; the area immediately to the east of the city is the San Francisco Bay). In contrast to San Francisco, San Jose to the south and east experiences higher ozone concentrations. Key differences include: (1) winds blowing into San Jose are already polluted with neighboring areas' emissions (for example, the southern portion of the San Francisco Bay Area, near San Jose, provides transported pollutants from upwind portions of the Bay Area including San Francisco and East Bay cities such as Oakland) and (2) San Jose is bordered by heavily developed areas with significant emissions activity.

In general, **Figures 3-3** (**a** and **b**) and **3-4** (**a** and **b**) show that the distribution of the 1-hour and 8-hour exceedances are relatively similar. However, at several of the downwind sites (e.g., Bethel Island and Livermore) there were considerably more 8-hour exceedances compared to 1-hour exceedances. While these sites have some local emissions that may contribute to their ozone concentrations, ozone transport from the San Francisco Bay Area is likely. This simple analysis shows that the area of influence of an urban area such as San Francisco may be greater for the 8-hour standard compared to the 1-hour standard. Therefore, monitoring networks for the 8-hour standard may need to consider larger geographic areas.

The effects of downwind transport can be graphically illustrated with the ozone data from the San Francisco Bay Area. Downwind sites can be more prone to exceedances of a 0.08 ppm 8-hour threshold due to transported pollutants that increase ozone concentrations in the early evening hours. This increased exceedance count can be explained in part by the diurnal ozone concentration profile of the site. For example, **Figure 3-5** shows a comparison of the diurnal profile for Bethel Island (site #8) and Livermore (site #1) for July 27, 1995. Livermore exceeded the 1-hour standard 10 times during 1992-1995, and exceeded the 0.08 ppm 8-hour threshold 20 times. By comparison, Bethel Island only exceeded the 1-hour standard one time during 1992-1995, but it exceeded the 0.08 ppm 8-hour threshold nine times. The diurnal profiles for both sites are very similar in the morning hours until about 10:00 a.m. After 10:00 a.m., the concentration at the Livermore site continues to rise rapidly, while the concentration at Bethel Island levels off. After about 2:00 p.m., the concentration at Livermore declines sharply, while the Bethel Island concentration actually rises to its peak at 6:00 p.m. For the remainder of the evening, the

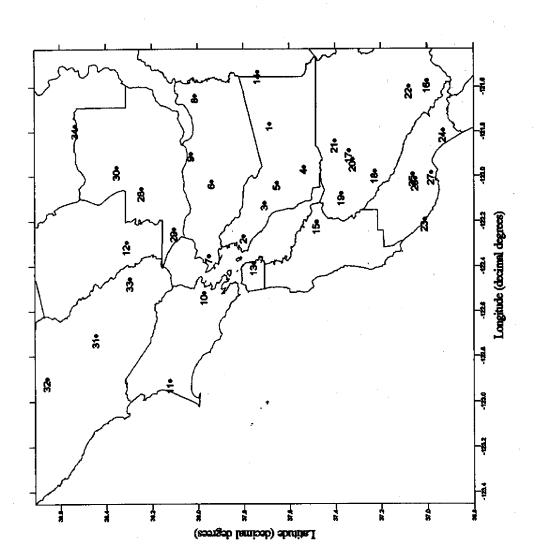


Figure 3-2. Selected monitoring sites that operated in the San Francisco Area and downwind regions bett 1992-1995.

Table 3-1. Monitoring sites in the San Francisco Bay Area and downwind regions. The number corresponds to the label used in Figure 3-2.

Number	City	County
1	Livermore	Alameda
2	Oakland	Alameda
3	San Leandro	Alameda
4	Fremont	Alameda
5	Livermore	Alameda
6	Concord	Contra Costa
7	Richmond	Contra Costa
8	Bethel Island	Contra Costa
9	Pittsburgh	Contra Costa
10	San Rafael	Marin
11	Point Reyes	Marin
12	Napa	Napa
13	San Francisco	San Francisco
14	Tracy	San Joaquin
15	Redwood City	San Mateo
16	Gilroy	Santa Clara
17	San Jose (4 th Street)	Santa Clara
18	Los Gatos	Santa Clara
19	Mountain View	Santa Clara
20	San Jose (Carlos Street)	Santa Clara
21	San Jose (Piedmont Rd.)	Santa Clara
22	San Martin	Santa Clara
23	Davenport	Santa Cruz
24	Santa Cruz (Airport Blvd.)	Santa Cruz
25	Scotts Valley (Vine Hill School Rd.)	Santa Cruz
26	Scotts Valley (Scotts Valley Dr.)	Santa Cruz
27	Santa Cruz (Bostwick Ln.)	Santa Cruz
28	Fairfield	Solano
29	Vallejo	Solano
30	Vacaville	Solano
31	Santa Rosa	Sonoma
32	Healdsburg	Sonoma
33	Sonoma	Sonoma
34	Davis	Yolo

Highest Number of 1-hour Exceedances Are Within the Eastern and Southern Portions of the San Francisco Bay Area

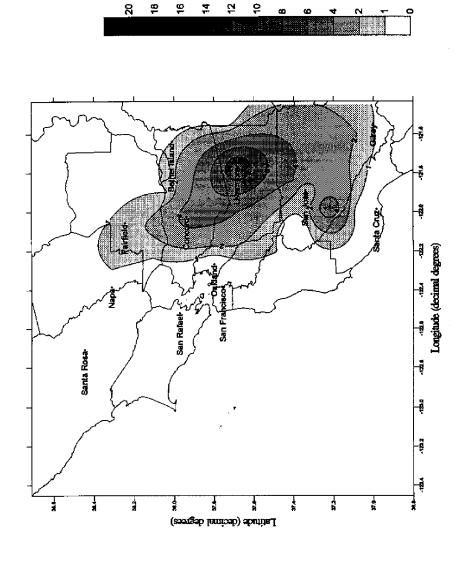
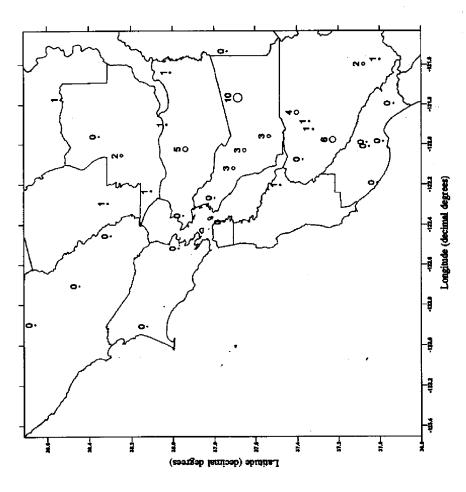
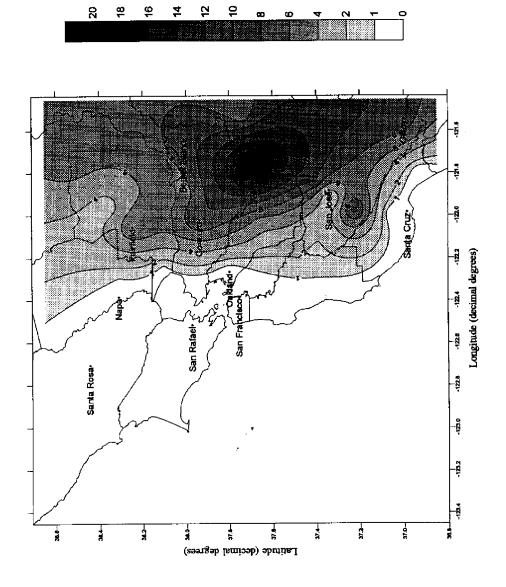


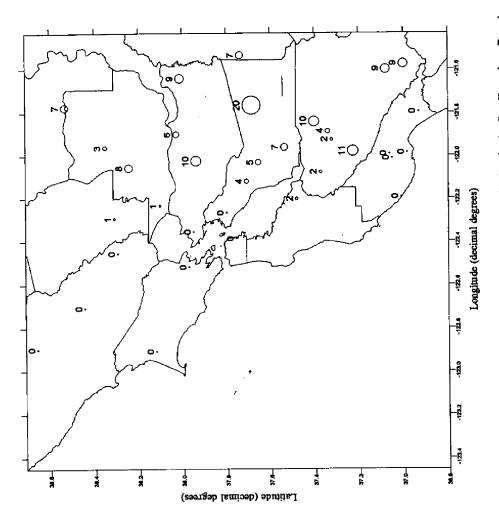
Figure 3-3a. Exceedances of the 0.12 ppm ozone threshold between 1992-1995 in the San Francisco Bay Area and downwind regions. The scale (0-20) represents the number of exceedances over the four-year period. The plot displays concentration differences among Bay Area and downwind monitor locations; the plot excludes several Sacramento sites around the northeast corner of the map.



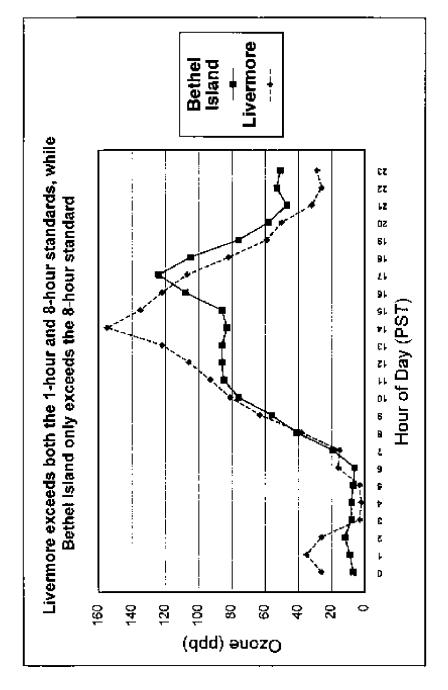
downwind regions. The size of the circles are proportional to the number of exceedances (which is shown above the circle). The plot displays data for the San Francisco Bay Area and downwind monitor locations; the plot excludes several Sacramento sites around the northeast corner of the map. Exceedances of the 0.12 ppm ozone threshold between 1992-1995 in the San Francisco Bay Area and Figure 3-3b.



Bay Area and downwind regions. The scale (0-20) represents the number of exceedances over the four year period. For the purposes of displaying differences between sites within the influence of emissions from the San Francisco Contour plot of the exceedances of the 0.08 ppm 8-hour threshold between 1992-1995 in the San Francisco Area, several Sacramento sites around the northeast corner of the map are not shown. Figure 3-4a.



downwind regions. The size of the circles are proportional to the number of exceedances (which is shown above the circle). The plot displays data for the SanFrancisco Bay Area and downwind locations; the plot Figure 3-4b. Exceedances of the 0.08 ppm 8-hour threshold between 1992-1995 in the San Francisco Bay Area and excludes several Sacramento sites around the northeast corner of the map.



Ozone concentration profiles for Bethel Island and Livermore for July 27, 1995. Livermore exceeds both the 0.12 ppm 1-hour and 0.08 ppm 8-hour thresholds. Bethel Island, a more rural site than Livermore, experiences lower mid-day ozone concentrations. An early evening rise in Bethel Island's ozone concentrations reflects transported pollutants from upwind areas. Transport on this day almost causes Bethel Island to exceed the 1-hour threshold, transport combined with locally generated ozone causes an 8-hour exceedance.

Figure 3-5.

concentration at Bethel Island is higher than at Livermore. Livermore exceeded both the 1-hour and 8-hour standards on this day, while Bethel Island only exceeded the 8-hour standard.

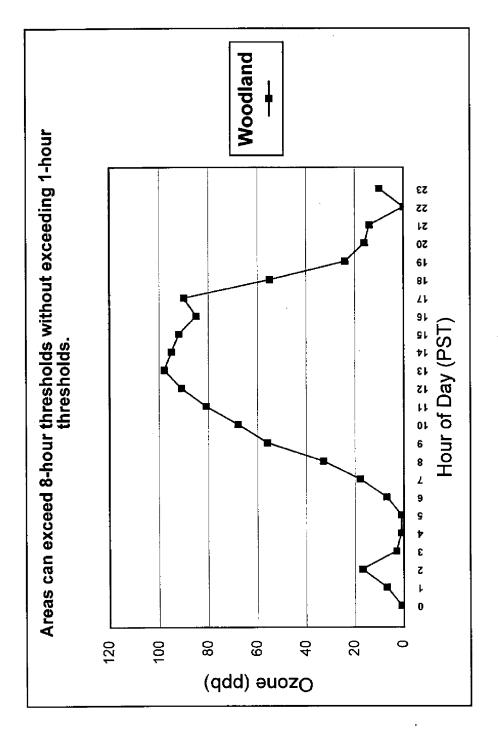
Both Livermore and Bethel Island receive transported ozone and ozone precursors from the urbanized areas to the west. However, the difference is likely explained by the difference in urbanization between Livermore and Bethel Island. Neither are very urban compared to San Francisco and San Jose, but Livermore is a moderately sized community near a major Interstate, which connects with Oakland; Bethel Island is a more rural site and not near any major roadways. Livermore likely has some ozone buildup in the afternoon as the result of local emissions to add to the transported ozone and ozone precursors, and the rush hour traffic provides fresh NO to quickly titrate the ozone concentration after the peak is reached in the late afternoon. Bethel Island likely receives a dispersed plume of ozone late in the afternoon, adding to ozone formed locally. Unlike Livermore, there is no late afternoon source of fresh NO to titrate the ozone; therefore, the ozone concentration lingers for a longer number of hours than at Livermore. The more elongated peak and the lingering of the ozone through the early evening at Bethel Island make this site more prone to 8-hour exceedances than Livermore. This suggests that for an 8-hour form of the standard, special attention needs to be given to rural sites receiving transported ozone without fresh NO in the late afternoon to titrate the ozone.

Rural or suburban areas that do not exceed 1-hour ozone thresholds can exceed 8-hour ozone thresholds. One example of this is the ozone concentrations monitored at Woodland, California. Woodland is a rural site located northeast of the San Francisco Bay Area, not far from the Sacramento metropolitan area. **Figure 3-6** shows ozone concentrations at Woodland on August 20, 1995. This site did not exceed the 0.12 ppm 1-hour ozone threshold from 1991 through 1995, but exceeded the 0.08 ppm 8-hour threshold 10 times during this period. The plot shows the concentration was above 80 ppb for 8 hours, without ever going above 100 ppb. Thus, this site has a steady ozone concentration throughout the afternoon, without reaching a high peak. This type of site is more likely to exceed a standard based on an 8-hour running average set at 0.08 ppm rather than the 1-hour peak concentration of 0.12 ppm.

3.1.2 Northeastern United States

The northeastern United States includes many major metropolitan areas and has been designated as an ozone transport region (OTR). In this section, spatial ozone patterns are presented for the entire OTR, including many metropolitan areas as well as rural areas which are influenced by ozone transport. The OTR in the northeastern United States extends from Virginia to Maine and contains several large metropolitan areas, including Washington, D.C., Baltimore, Philadelphia, New York City, and Boston. **Figure 3-7** presents a map of the OTR showing the location of all of the major cities. The close proximity of these cities along a southwest to northeast line and a generally southerly or southwesterly flow in the summertime ozone season results in a complex interaction of ozone and ozone precursors in the region.

Figures 3-8 and **3-9** depict the spatial pattern of exceedances of the 0.12 ppm 1-hour ozone threshold for 1988 and 1995. These years were chosen for display because in the northeast and nationwide, 1988 was the year with the highest number of ozone exceedances in the 1980s and 1990s, and 1995 is the most recent year (as of this writing) with available ozone data. **Figures 3-10** and **3-11** show



Ozone concentration profile for Woodland, California (northeast of the San Francisco Bay Area) on August 20, 1995. Under the conditions experienced on this day, Woodland exceeded the 0.08 ppm 8-hour threshold without exceeding the 0.12 ppm 1-hour threshold. Figure 3-6.

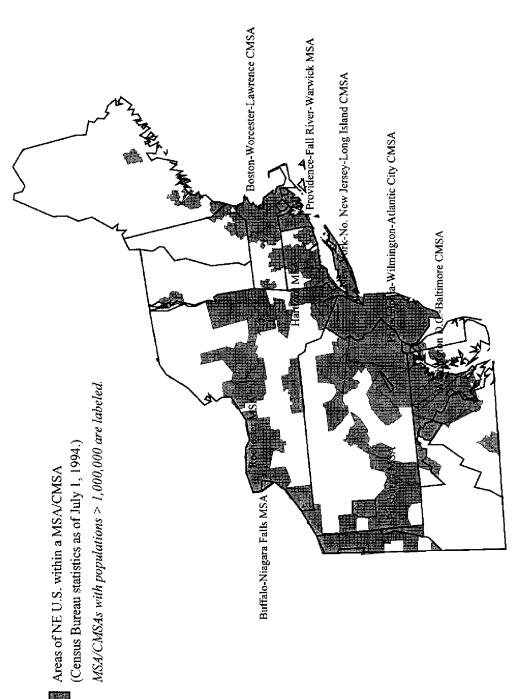


Figure 3-7. Major cities in the Northeastern United States.

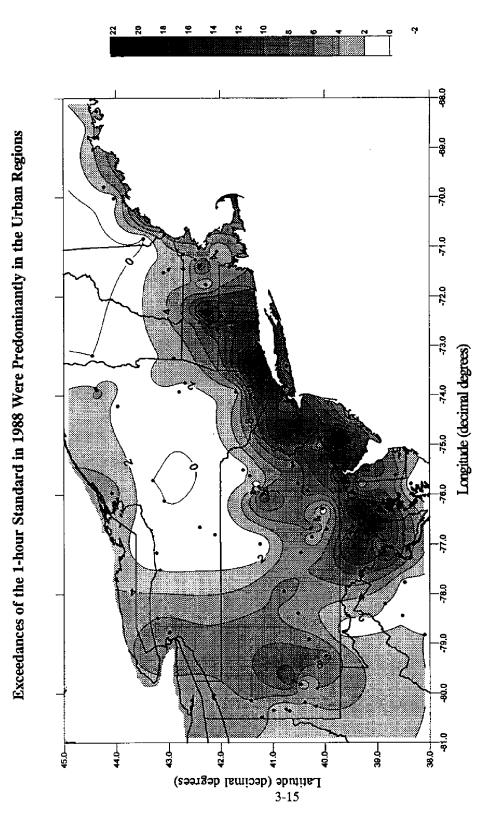


Figure 3-8. Number of site exceedances of the 1 hour 0.12 ppm ozone threshold (greater than or equal to 125 ppb) in the Northeast OTR during 1988. Monitoring sites are represented by the black dots.

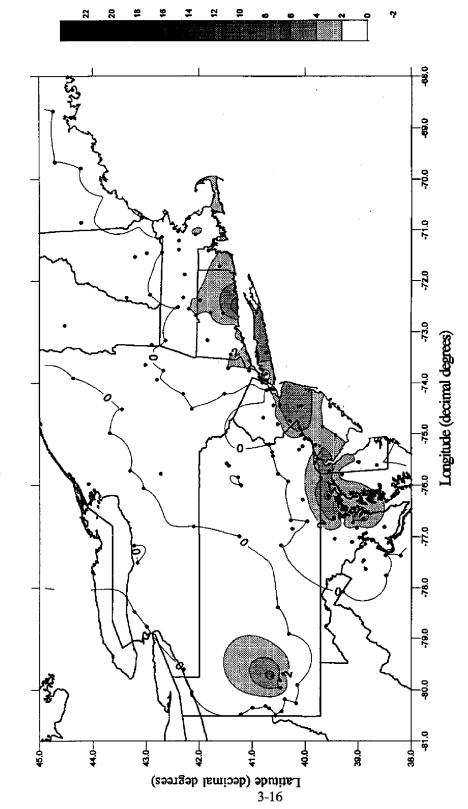


Figure 3-9. Number of site exceedances of the 1 hour 0.12 ppm ozone threshold (greater than or equal to 125 ppb) in the Northeast OTR during 1995. Monitoring sites are represented by the black dots.

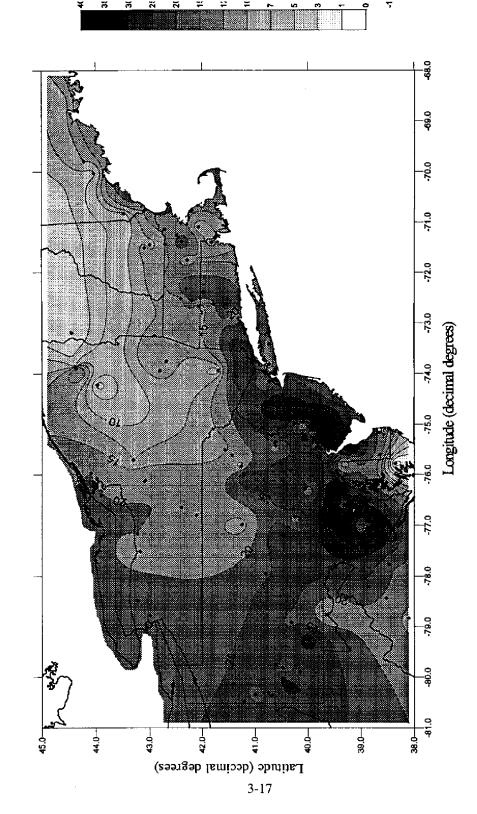


Figure 3-10. Number of site-exceedances of the 0.08 ppm 8-hour running average in the Northeast OTR during 1988. Monitoring sites are represented by the black dots.

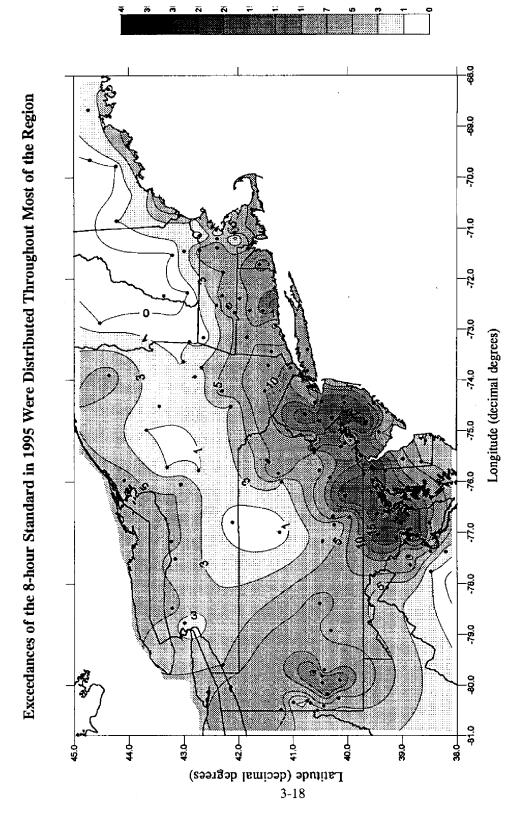


Figure 3-11. Number of site-exceedances of the 0.08 ppm 8-hour running average in the Northeast OTR during 1995. Monitoring sites are represented by the black dots.

contour plots of the number of exceedances of the 0.08 ppm 8-hour threshold for 1988 and 1995. For both the 1-hour and 8-hour indices, there are a high number of exceedances in the Baltimore-Washington D.C. area, Philadelphia, and New York City. Areas such as Maine and western Pennsylvania also recorded a significant number of exceedances. The exceedances in Maine are likely the result of transport from the metropolitan areas of Boston and New York. Note that there are significantly more exceedances of the 8-hour standard than the 1-hour standard in the rural areas.

Husar (1996) conducted a similar analysis for the Ozone Transport Assessment Group (OTAG) region, which includes 37 eastern states. In Husar (1996) the spatial pattern of exceedances of the 0.12 ppm 1-hour threshold and the 0.08 ppm 8-hour running average were compared from 1991-1995 (June through August). Over the entire OTAG region, the mean 8-hour average was 86 percent of the 1-hour daily maximum. Husar (1996) concluded that switching from a 0.12 ppm 1-hour NAAQS to a 0.08 ppm 8-hour NAAQS would yield an increase in exceedances over the industrial midwestern states from Illinois to Pennsylvania and a decrease of exceedances around Houston and New York City. However, the overall exceedance pattern of the 1-hour and 8-hour indices were very similar. Additionally, Husar (1996) examined the correlation between the 1-hour and 8-hour concentrations among monitoring sites. The correlation coefficient was extremely good (r²=0.96). Husar (1996) shows that there are only subtle differences in the exceedance patterns of the 1-hour and 8-hour forms of the standard on a regional basis.

To further examine the subtle differences between the 1-hour and 8-hour forms, contour plots of the ratio of the 8-hour maximum ozone concentration and the 1-hour maximum ozone concentration were computed for several high ozone concentration days. The significance of the 8-hour/1-hour ratio is that higher values tend to indicate that a site is more prone to 8-hour exceedances, and lower values tend to indicate that a site is more prone to 1-hour exceedances. Figures 3-12 and 3-13 show plots of this ratio for two regional ozone episodes in the northeastern United States (i.e., ozone exceedances were observed throughout the OTR on June 15, 1988, and July 20, 1991). Typically, the 8-hour/1-hour ratio is lower in the center of metropolitan areas. The figures show low ratios in Washington D.C. and New York City with the ratio increasing with distance from the city centers. This effect is likely a result of NO titration of ozone during the morning and afternoon rush hours, which prevents sustained high concentrations of ozone in the metropolitan areas. Downwind sites away from cities receive transported ozone and ozone precursors from cities. There is less NO to titrate the ozone in the rural and suburban areas outside of the cities. For downwind sites that are far from any cities, the transported ozone plume is likely to be spatially dispersed, resulting in flatter diurnal profiles. Areas such as western Pennsylvania, upstate New York, and Maine had high values of the ratio, illustrating this effect. These are areas which receive transported ozone (likely from dispersed plumes) and have low NO concentrations available for titration. This effect points to the increased importance of rural ozone monitoring outside the urban/suburban core for measuring 8-hour concentrations as compared to 1-hour values.

3.2 SUMMARY AND CONCLUSIONS

The following general observations can be made from the analysis of the San Francisco and northeastern United States ozone concentrations:

- The locations of the exceedances of the 0.12 ppm 1-hour and the 0.08 ppm 8-hour average ozone thresholds were generally similar, with some exceptions.
- The locations of the maximum concentration during exceedances were generally similar for the 1-hour and 8-hour thresholds within the San Francisco Bay Area, however, far downwind sites were more prone to 8-hour exceedances relative to 1-hour exceedances. Therefore, the geographic scope of ozone monitoring for an urban area may need to be expanded for the 8-hour threshold.
- Differences between the 1-hour and 8-hour ozone values among sites can partially be explained by the ozone diurnal profile at the sites. For example, downwind sites which receive transported, dispersed ozone plumes and have low NO concentrations available to titrate ozone will have flatter diurnal concentration profiles and are more prone to 8-hour exceedances, relative to 1-hour exceedances.
- The ratio of the 0.08 ppm 8-hour running average to the 1-hour maximum concentration increased with distance from the center of the major cities on episode days. In other words, as you move away from the center of major cities, the outlying areas become more prone to exceeding the 0.08 ppm 8-hour threshold rather than experiencing peak 1-hour concentrations. Some of the highest values of this ratio were observed in areas outside the urban/suburban core.

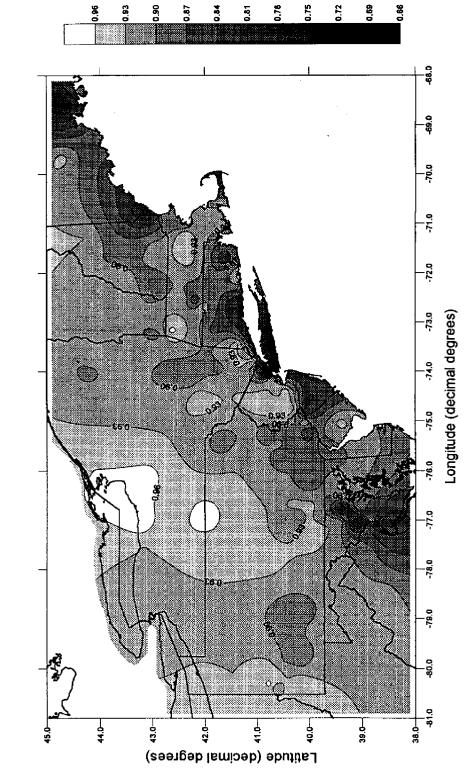
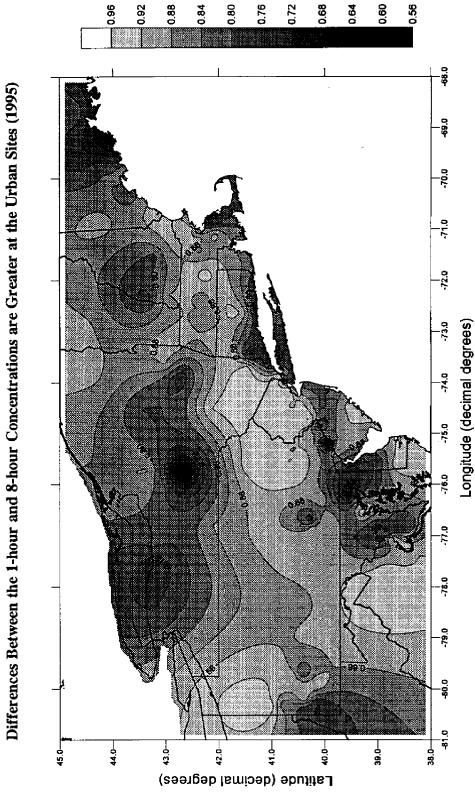


Figure 3-12. Ratio of the concentration of the 0.08 ppm 8-hour running average standard and the 1 hour 0.12 ppm ozone threshold for the ozone episode of July 20, 1991. Higher values tend to indicate a site is more prone to 8-hour exceedances; lower values indicate the site is more prone to 1-hour exceedances.



Ratio of the concentration of the 0.08 ppm 8-hour running average standard and the 1 hour 0.12 ppm ozone threshold for the ozone episode of July 15, 1995. Higher values tend to indicate a site is more prone to 8-hour exceedances; lower values indicate the site is more prone to 1-hour exceedances. Figure 3-13.

4. MONITORING OBJECTIVES AND NETWORK DESIGN

4.1 INTRODUCTION

EPA requires different monitoring efforts depending upon an area's nonattainment status. In general, the more polluted and populous a region is, the more extensive the required monitoring. For ozone, there are two monitoring network systems: (1) the State and Local Air Monitoring Stations (SLAMS), and (2) the National Air Monitoring Stations (NAMS). The objectives of the SLAMS network are (CFR, 1997):

- Determine the highest concentrations expected to occur in the area covered by the network.
- Determine representative concentrations in areas of high population density.
- Determine the impact on ambient pollution levels of significant sources or source categories.
- · Determine general background concentration levels.

The SLAMS stations are used to determine compliance with the ozone NAAQS. The EPA does not specify the number of required stations, except to prescribe a minimum number of stations (see Section 4.3). States and localities are given flexibility in determining the size of their network based on data needs and available resources.

The NAMS stations are selected from the SLAMS stations. Thus, the NAMS network is a subset of the SLAMS network. Areas to be monitored must be selected based on urbanized population and pollutant concentrations. Accordingly, there are two categories of NAMS monitors: (1) stations located in areas of expected maximum concentrations, and (2) stations which combine poor air quality with a high population density but are not necessarily located in an area of expected maximum concentrations (sometimes referred to as the maximum exposure monitor). The NAMS monitors are designed to provide data for national policy analyses and trend analyses, and for providing the public with information about the air quality in major metropolitan areas. Therefore, it is intended that these stations remain at the same location. The criterion for designating NAMS sites is any urban area with a population over 200,000. A minimum of two NAMS monitors are required in each of these urban areas.

In addition, serious, severe, and extreme ozone nonattainment areas are required to implement enhanced ozone monitoring. This enhanced monitoring is called the Photochemical Assessment Monitoring Stations, or PAMS program. PAMS requirements are extensive; including them in this report would complicate the effort to provide a primer on 1-hour and 8-hour ozone monitoring. Appendix B includes PAMS references for readers seeking PAMS guidance materials.

This section describes the issues that determine what type of monitoring network is appropriate for a given metropolitan area. Specific topics covered include:

· Monitoring principles involving localized versus regional scale monitoring.

- Monitoring objectives, such as the need to demonstrate compliance with federal air quality standards, and how they relate to monitor placement.
- · Seasonal monitoring requirements.

4.2 PRINCIPLES INVOLVING LOCALIZED VS. REGIONAL MONITORING

As a secondary pollutant, ozone requires appreciable formation time; longer time periods allow precursor emissions to distribute more uniformly across a region, and thus allow ozone concentrations to develop more uniformly across subregions and even large-scale regions. This does not imply that ozone concentrations do not vary across a metropolitan area, it simply means that the gradient in ozone concentrations is not as great as some other pollutants that derive directly from emission sources. For example, carbon monoxide can reach significantly high concentrations in localized "hot spots" such as busy intersections. High ozone concentrations generally occur over larger areas.

In contrast to ozone concentrations, ozone precursor emissions can vary significantly in small areas. Monitoring, depending upon whether it is done for ozone or emissions precursors, needs to reflect an understanding of the spatial scale over which precursor emissions and ozone concentrations occur. Given the importance of large-scale transport in the ozone formation process, meteorological conditions are particularly important to the site selection process. For monitoring secondary pollutants, one must identify areas generally downwind of the primary pollutant sources during periods conducive to formation of the secondary pollutant. It is important to consider the winds, in combination with the length of time it takes ozone to form, and the locations of the major sources of the reactants. These factors will be useful for determining where in an urban region the maximum ozone concentration occurs. Since the mixing of the ozone precursors will occur over a large volume of air, the monitoring of small-scale variability is usually not necessary for ozone.

Given these principles, four types of spatial scales can be defined for ozone and ozone precursor monitoring (40 CFR Part 58, Appendix D; CFR, 1997):

- Middle-Scale: Measurements at this scale represent conditions close to the sources of VOC and NO_x emissions such as roads where it would be expected that suppression of ozone concentrations would occur. Trees may also have a strong scavenging effect on ozone concentrations and may tend to suppress ozone concentrations in their immediate vicinity. Measurements at these stations would represent conditions over relatively small portions of the urban area.
- Neighborhood: Measurements in this category represent conditions throughout some reasonably homogeneous urban subregion, with dimensions of a few kilometers. These types of stations are useful for the assessment of health effects because they represent conditions in areas where people work and live. These sites, if also monitoring for ozone precursors such as VOC or NO_x, are useful for understanding sources of ozone precursors.

- *Urban:* This measurement scale is useful for quantifying concentrations over very large portions of a metropolitan area with dimensions of 50 or more kilometers. Such measurements can be used for determining trends, and designing area-wide control strategies. The urban-scale sites can also be used to measure high concentrations downwind of the area having the highest precursor emissions.
- Regional: This scale of measurement can be used to represent concentrations over large portions of a metropolitan area and even larger rural areas with dimensions of as much as hundreds of kilometers. Data from such sites can be useful for assessing the ozone that is transported into or out of an urban area. Also, data from such stations can be useful for quantifying the amount of ozone and ozone precursors that cannot be reduced by control strategies within that urban area.

4.3 MONITORING OBJECTIVES AND SITE SELECTION

The data from an ozone monitoring network serves a myriad of purposes. Regulators use the data to determine compliance with the ozone NAAQS; compliance with the NAAQS determines which, if any, control strategies are necessary. Some metropolitan areas use ozone monitoring networks to warn residents when unhealthy ozone concentrations are expected. A detailed understanding of the spatial and temporal distribution of ozone is needed for researchers that develop models to simulate the atmosphere. These models can be used by regulators in the development of control strategies or by researchers trying to better understand atmospheric chemistry, meteorology, and the relationship between emission precursors and ozone formation. Yet another purpose of the ozone monitoring network is for human exposure assessment. Researchers conducting health studies need to estimate the exposure of residents to ozone and other pollutants in both high and low concentration areas. Exposure is generally best estimated by sites close to where people live, work (particularly for outdoor workers), and play (e.g., school playgrounds).

The EPA (CFR, 1997) lists the major objectives of ozone monitoring:

- Determine the highest concentrations expected to occur in the area covered by the network.
- · Determine representative concentrations in areas of high population density.
- Determine the impact of ambient pollution levels of significant sources or source categories.
- Determine general background levels. This can mean the natural background level or the concentration of the pollutant upwind of the area from sources outside the area.

This suggests four major types of monitoring sites: (1) maximum downwind concentration sites, (2) maximum exposure sites, (3) maximum emissions sites, and (4) upwind sites. These site types are summarized in **Table 4-1**. Additional monitoring objectives are:

- Determination of human exposure for health effect studies.
- · Data for air quality research studies.
- · Impact on vegetation.

Table 4-1. Ozone and ozone precursor monitoring site types with corresponding monitoring objectives.

Type of Site	Relevant Pollutants	Monitoring Objective ^a	Spatial-Scale	Notes
Maximum Downwind Concentration	Ozone	Regulatory Compliance	Urban to Regional	This site is required as part of the NAMS network and is designed to measure the maximum ozone concentration in an urban area.
Maximum Exposure	Ozone	Regulatory Compliance	Neighborhood to Urban	This site is required as part of the NAMS network and is designed to measure the highest concentration in a heavily populated area.
Maximum Emissions	NO _x , VOC ^b	Control Strategy Development	Middle-Scale	This site is designed to measure the concentration of NO and VOC in proximity to a source. This data would be used in modeling ozone formation.
Upwind	Ozone, NO _x , VOC ^b	Control Strategy Development	Regional	This site is designed to measure the ozone and ozone precursor concentrations entering an urban area from an upwind source region.
Exposure	Ozone	Data for Health Studies	Neighborhood to Urban	This site provides additional (i.e., more than the maximum exposure site required for NAMS) exposure data for health studies.
Vegetation	Ozone	Measure Impact to Vegetation	Urban to Regional	This site is used to quantify the exposure of vegetation to ozone to assess the deleterious impact on the vegetation.
Research	Ozone, NO _x , VOC	Research	Middle-Scale to Regional	This site is established for a specific research purpose independent of regulations. Often these sites will operate only temporarily (i.e., during a single summer season).

^a For all MSAs or CMSAs with more than 200,000 people, two NAMS sites are required, the maximum downwind site and the maximum exposure site. If the MSA/CMSA is a serious, severe, or extreme nonattainment area; up to five sites are required. (Note that PAMS sites are based on population - see 40 CFR Part 58, Appendix D, Table 2.) The EPA does not have specific rules on the placement of these additional SLAMS sites.

Additional downwind, exposure, and emission sites can be installed as necessary, or as resources permit. Definitions of the spatial scale and type of monitoring site are found in 40 CFR Part 58, Appendix D, "Network design for SLAMS, NAMS, and PAMS."

^b EPA requires PAMS VOC monitoring for serious, severe, and extreme ozone nonattainment areas. Up to two of the NAMS monitors may be part of the PAMS program in these areas. Appendix B to this document includes references for additional information on PAMS monitoring.

These different monitoring objectives require different site selection criteria. The remainder of this section describes how these different objectives affect site selection.

4.3.1 Regulatory Compliance

For regulatory compliance, the principle objective is to measure the ozone concentration in the high population areas and the downwind concentration from the urban region. It is important to be careful when selecting the high population sites because, particularly in dense urban areas, the greatest concentration of people may be in an area with heavy automobile traffic, which may result in low ozone concentration due to NO titration. Therefore, the high population sites must be chosen by considering both population and the level of nearby fresh NO_x emissions. Generally, the area with the highest population density that might be reasonably exposed to a significant ozone concentration should be chosen. (Section 5. discusses strategies for determining where the maximum downwind concentration is located.) For areas requiring more than two ozone monitoring sites, additional monitors can be placed in other areas downwind of the urban region (other than the maximum concentration downwind area) that may receive transported ozone on a particular day.

4.3.2 Control Strategy Development and Assessment

Another important objective for monitoring is the development of control strategies. This requires monitoring of both ozone and ozone precursors. For ozone, the sites for regulatory compliance will be useful for this purpose, as well as additional downwind sites. However, an additional site type is critical for control strategy development; monitors should be placed upwind of the urban area to determine the concentration of ozone and ozone precursors entering the urban region. This will help to determine what portion of an area's ozone problem is due to local emissions and what portion is due to transported ozone and ozone precursors. It is also important to measure NO_x and VOC concentrations for control strategy development. In particular, NO_x and VOC monitors should be placed near the major NO_x and VOC source regions, which are normally in the areas within the urbanized portion with the highest vehicle traffic. Note that EPA has prepared separate guidance concerning VOC monitoring. EPA has, for example, detailed enhanced monitoring requirements for serious, severe, and extreme ozone nonattainment areas, and these requirements provide for the monitoring of over 50 individual VOC species. Appendix B to this document includes references for those interested in learning more about VOC monitoring.

4.3.3 Health Effect Studies

For health effect studies, the emphasis is on neighborhood-scale monitors which can be used to quantify the exposure of the residents of a particular community. Typically, the more differentiation one can make in the exposure of residents within an urban area, the more statistical power there is to detect any health effects that may be associated with the exposure. Therefore, areas with good monitor coverage are ideal for health effect studies.

4.3.4 Vegetative Impacts Related to a Secondary Ozone Standard

Secondary standards relate to ecological and welfare effects, as opposed to health effects. Since ozone adversely affects vegetative growth (e.g., commercially produced crops as well as natural forests), additional regional-scale monitors for vegetation may be necessary. Information on monitoring network design to address ecological effects is provided by Reiss et al., 1995. Generally, Class I areas and areas with a large density of agriculture are important areas for monitoring the effects for the secondary standard.

4.4 OZONE SEASON

For the purposes of regulatory monitoring, an ozone season is defined for each state and dominion in the United States. This ozone season is defined as the period for which exceedances of the standard are expected. Monitoring for ozone is only required during this season. The EPA recently sponsored an update to the existing ozone season definitions (U.S. EPA, 1998) to better reflect the ozone season for the 0.08 ppm 8-hour threshold. The methodology used to determine the new ozone seasons includes points such as (U.S. EPA, 1998):

- 1. 8-hour average ozone concentrations were calculated by the U.S. EPA for each day and station in the United States and its territories using hourly data from the Aerometric Information Retrieval System (AIRS) database; the EPA provided this data for the six-year period 1990-1995.
- 2. For determining the ozone season for 8-hour averaging times, exceedances of the 0.080 ppm threshold for each station-month were computed.
- 3. These data were used to construct state-by-state histograms for the months in which the 8-hour concentrations were greater than 0.080 ppm in the six-year period 1990-1995 using all available data for each state.
- 4. Initial ozone seasons for each state were defined as the first month with any daily 8-hour concentration greater or equal to the 0.080 ppm threshold, and ending with the month when the last exceedances of the 0.080 ppm threshold occurred.

With an 8-our season adjustments to these initial ozone seasons are expected to better reflect the need for similar ozone monitoring seasons within ozone transport areas; and to consider states with large geographic areas without available ozone data. Ozone seasons for major metropolitan areas, as well as a complete description of the methodology used to define these seasons, can be found in U.S. EPA (1998).

5. MACROSCALE CONSIDERATIONS IN MONITOR SITING

5.1 DEVELOPMENT OF A NEW NETWORK OR ENHANCEMENT OF AN EXISTING NETWORK

This section provides guidance on the siting of four major types of monitors that are needed in an ozone monitoring network. As discussed in the last section, these sites are:

- 1. Maximum downwind concentration sites
- 2. Maximum population exposure sites
- 3. Maximum emissions sites
- 4. Upwind sites

In addition, this section presents how these monitoring site types are typically deployed to measure maximum ozone concentrations under two meteorological scenarios: (1) During conditions when transport occurs from upwind sources or polluted regions (maximum ozone concentration is often determined by the direction of winds from the emission sources, thus the maximum ozone concentration often occurs along the path of the predominant wind direction); and (2) during stagnant conditions when ozone forms primarily from local emission sources.

5.1.1 Maximum Population Exposure Site(s)

This site is fairly straightforward to locate. Census tract data or other population data may be used to locate the maximum population area. However, care must be given not to locate this monitor in an area which is too heavily influenced by local emission sources, given the titration of ozone by nitric oxide, which is part of fresh industrial emissions or automobile exhaust. Therefore, this monitor should be located in the area with the highest population that is expected to be exposed to a relatively high ozone concentration. This area is likely to be located on the urban fringe in an suburb slightly downwind of the urban area.

5.1.2 Upwind and Downwind Site(s)

As discussed before, ozone forms in the atmosphere by reactions between VOC and NO_x. These reactions take some time to occur, thus the maximum ozone concentration usually occurs 4 to 6 hours after maximum emissions, and under conditions of light winds, usually downwind of the urban region (U.S. EPA, 1978; Chu, 1995). Therefore, the key factor for identifying the area where the maximum ozone concentration is expected to occur is to determine the principal wind direction (PWD) from the urban area. Also, the most significant amount of transported ozone and ozone precursors will come from the area where the winds enter the city. As meteorological conditions influence the formation of ozone, it is important to consider PWDs on days when the ozone standard is violated or, if there is no existing network, on days when conditions are expected to be conducive to ozone formation.

This point is illustrated in **Figure 5-1**, which shows the morning wind roses for Muskegon, Michigan from 1981 through 1990 for summer days (June-September) that exceeded the 0.12 ppm 1-hour ozone threshold, as well as for all summer days. Wind roses should be interpreted as follows:

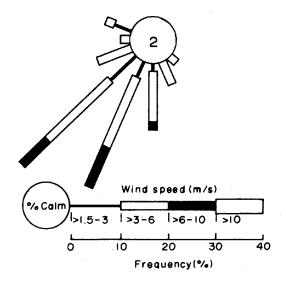
- The arms of the roses point to where the wind was coming from.
- The length of the arm is proportional to the percentage of time that the wind was coming from that direction.
- The various pieces of the arm represent speed categories.

A program to construct wind roses is available from the EPA Technology Transfer Network (TTN), which is operated by the EPA's Office of Air Quality Planning and Standards (OAQPS) in Research Triangle Park, North Carolina. Within TTN, the Support Center for Regulatory Air Models (SCRAM) provides a program which constructs wind rose plots from user-provided meteorological data. Appendix B to this document includes references directing the reader on how to access the TTN and other relevant EPA information.

As shown in **Figure 5-1**, there is no distinctive morning PWD for Muskegon if all the summer days are included. However, for days with peak ozone levels above the 0.12 ppm 1-hour threshold, the majority of winds come from the southwest. Thus, for Muskegon, an upwind monitor should be placed to the southwest and similarly, the downwind maximum ozone site should be located based on an afternoon exceedance day wind rose. Therefore, when determining the appropriate downwind location for an ozone monitor, it is important to concentrate on the meteorological conditions present during an exceedance day. Given the generally good correlation between the 0.12 ppm 1-hour and the 0.08 ppm 8-hour thresholds, it is expected that historical information describing prevailing wind direction during 1-hour exceedance conditions will generally still be valid during 8-hour exceedances.

For areas without existing monitoring data or areas which are not certain if their monitors are located in the maximum downwind direction, Chu (1995) has developed a methodology for determining from meteorological data which days were most conducive to ozone formation. The methodology is based on the model developed by Cox and Chu (1993) for relating meteorological variables to the ozone concentration. Cox and Chu (1993) have found that the maximum ozone concentration is best correlated with the following meteorological variables: (1) daily maximum 1-hour temperature, (2) morning (7-10 a.m.) winds, (3) afternoon (1-4 p.m.) winds, and (4) midday (10 a.m.-4 p.m.) relative humidity (RH). Using these relationships, Chu developed a set of meteorological conditions that are likely to occur during a day that exceeds the NAAQS. These conditions are summarized in **Table 5-1**. **Figure 5-2** depicts the latitude delineations used in **Table 5-1**. The data used to develop these relationships were based on 31 eastern cites, but the relationships were found to be adequate for the entire United States. These criteria were developed based on the 0.12 ppm 1-hour NAAQS. However, the general correlation between the 1-hour and the 8-hour ozone thresholds suggests that the 1-hour relationships should be generally applicable during 8-hour conditions. Nonetheless, it would be useful to re-evaluate and possibly refine the criteria using the 8-hour threshold.

Muskegon am windrose (ozone GE 120 PPB)



Muskegon am windrose (summertime)

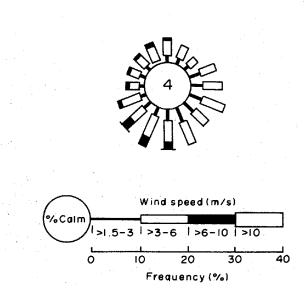


Figure 5-1. Morning wind roses (7-10 a.m.) for Muskegon, Michigan from 1981-1990 for summer days (June-September) for (a) days that exceeded the 0.12 ppm 1-hour ozone threshold, and (b) all days (Chu, 1995). The figure illustrates that prevailing winds on ozone exceedance days can be distinct from average wind conditions.

Table 5-1. Criteria for ozone conducive conditions for the eastern United States.

1. T ³ 26.5°C (79.7°F) for cities north of 40°N T ³ 29°C (84.2°F) for cities between 35°N and 40°N T ³ 32°C (89.6°F) for cities south of 35°N

2. $W_{a.m.}$ £ 5 m/s for cities in transport regions (i.e., Midwest and Northeast) $W_{a.m.}$ £ 4 m/s for cities outside transport regions.

3. $W_{p.m.}$ £ 7.5 m/s for cities in transport regions $W_{p.m.}$ £ 6 m/s for cities outside the transport regions $W_{p.m.}$ £ 5 m/s for Gulf Coast cites and Florida

4. RH £ 75% for coastal cities north of 40°N RH £ 65% for inland cities between 30°N and 40°N RH £ 70% for all cities south of 30°N.

Source: Chu, 1995.

Notes: T refers to temperature; W refers to wind speed; RH refers to relative humidity.

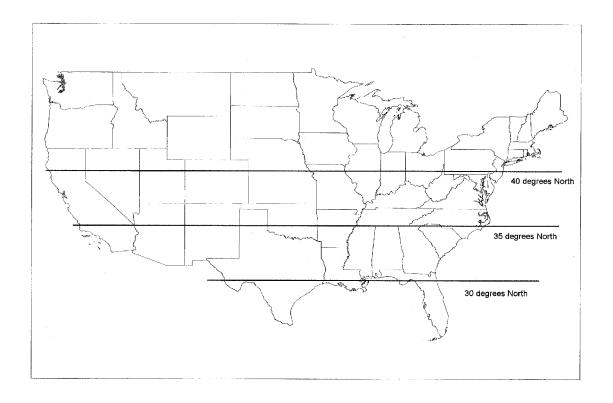


Figure 5-2. Depiction of the 30, 35, and 40 degree latitude lines for the United States

After determining the ozone conducive days over the analysis period, wind roses should be calculated for the morning (7-10 a.m.) and afternoon (1-4 p.m.) for these days. The morning wind rose will be used to determine the location of upwind monitors, and the afternoon wind rose will be used to determine the location of downwind ozone monitors. Sometimes the morning and afternoon wind roses can be different. However, over simple terrain areas, the morning and afternoon wind roses and corresponding PWDs are usually similar except for some urban heat island effect which creates a deflection immediately downwind of the city. Over complex terrain and over coastal areas, the two wind roses can be different. This is illustrated in **Figures 5-3** and **5-4**, which show the morning and afternoon wind roses for Milwaukee, Wisconsin and Atlanta, Georgia. While the morning and afternoon wind roses are similar in the flat terrain metropolitan area of Atlanta, the complex interactions between the synoptic winds and the mesoscale lake breeze of Lake Michigan are evident in the difference between the morning and afternoon wind roses be examined.

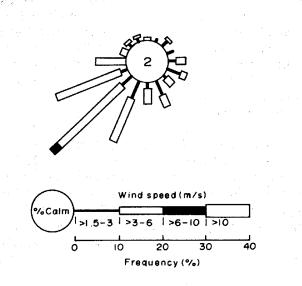
As an example, **Figure 5-5** shows a four-monitor PAMS/ozone network design for a metropolitan area. The sites in this sample monitoring design are as follows: (1) background ozone concentration (i.e., upwind site), (2) maximum precursor emissions site, (3) daily maximum ozone concentration (i.e., downwind site), and (4) ozone impact on downwind areas. The morning PWD was used as a guide for siting the background ozone concentration and maximum precursor emission sites, Sites #1 and #2. The afternoon PWD was used to site the ozone monitors, Sites #3 and #4, downwind of the metropolitan area. Chu (1995) recommends that Site #1 be located along the morning PWD upwind from the city limit near the edge of the photochemical grid model domain, and Site #2 should be located along the morning PWD near the downwind edge of the central business district (CBD). Site #3 should be located along the afternoon PWD at the location where the daily maximum ozone concentrations are likely to occur. For coastal cities, the site should be located as near as possible to the sea/lake breeze convergence zone.

For the 0.12 ppm 1-hour NAAQS, the maximum 1-hour ozone concentration is likely to occur in the early afternoon about 4 to 6 hours after the precursors are emitted. Therefore, the morning and afternoon wind roses can be used to find an approximate location of the maximum ozone concentration. For the 0.08 ppm 8-hour threshold, the maximum concentration generally occurs roughly in the same downwind area (or slightly further downwind) as the 1-hour daily maximum. Site #4 should be located along the afternoon PWD near the downwind edge of the photochemical grid model domain.

5.1.2.1 Stagnation Conditions

Chu (1995) notes that the approach described above is not applicable for ozone episodes occurring during extreme stagnation conditions (average winds < 1.5 m/sec) because, in some cases, no PWD can be resolved. However, for most stagnation dominated areas, distinct PWDs are still identifiable. As an example, morning wind roses are shown in **Figure 5-6** for two stagnation dominated metropolitan areas: Louisville, Kentucky and Huntington, West Virginia. While the winds in these cities are much lighter than the winds in the other cities that were shown, the light but steady winds in these cities appear to play an important role in the transport, mixing, and accumulation of pollutants.

Milwaukee am windrose (ozone GE 120 PPB)



Milwaukee pm windrose (ozone GE 120 PPB)

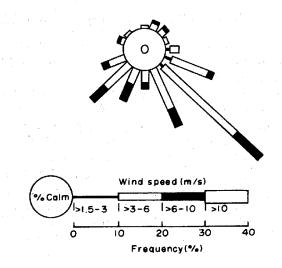
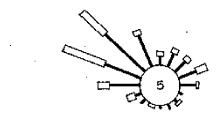
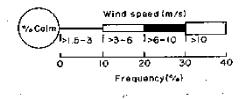


Figure 5-3. Morning (7-10 a.m.) and afternoon (1-4 p.m.) wind roses for Milwaukee, Wisconsin (Chu, 1995). The figure illustrates that in an area with complex terrain, wind patterns may shift during the day; therefore, upwind and downwind sites will not necessarily be located in a straight line through the region.





Atlanta am windrose (ozone conducive)

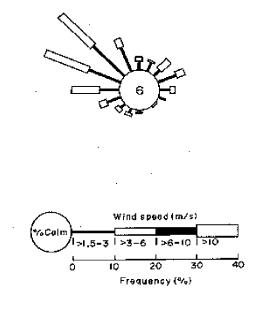
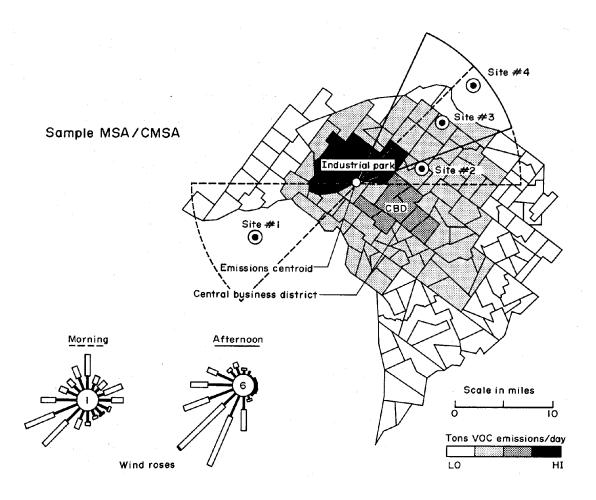


Figure 5-4. Morning (7-10 a.m.) and afternoon (1-4 p.m.) wind roses for Atlanta, Georgia (Chu, 1995). In contrast to the Milwaukee illustration, the Atlanta example illustrates that in an area with a relatively flat terrain, prevailing wind conditions may remain steady throughout the day. In this example, upwind and downwind monitors would be sited along a straight path through the region.



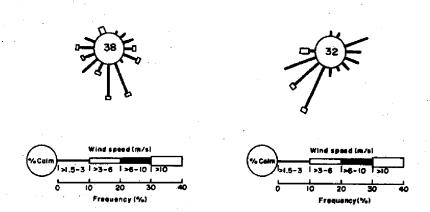


Figure 5-6. Morning wind roses (7-10 a.m.) for two stagnation dominated metropolitan areas: Louisville, Kentucky and Huntington; West Virginia (Chu, 1995). This illustrates that even with light winds, an area may still have a prevailing wind direction that affects the siting of upwind and downwind monitors.

For stagnation dominated areas where a well defined PWD may not be discernible, Chu (1995) recommends that the major axes of the precursor emission sources be substituted for PWDs. **Figure 5-7** shows an example PAMS/ozone monitoring network using this strategy. As shown, the axes of the emission sources extend across the industrial park and CBD. Chu (1995) recommends that monitors be located within 10 miles of the urban fringe (i.e., no further than 10 miles beyond the outermost portion of the urban fringe). The reasons for this choice are as follows: (1) completely calm conditions seldom last more than an hour during the day because most calm days have light variable winds, and (2) ozone concentrations are likely to be highest. He winds are along the axis of emissions because precursor concentrations are likely to be highest.

5.2 EXAMINATION AND ADJUSTMENT OF AN EXISTING OZONE MONITORING NETWORK TO REFLECT 8-HOUR MONITORING NEEDS

The need to monitor ozone during 8-hour running average periods raises the issue of whether monitoring networks designed around the 1-hour standard are adequate. The analysis presented in Section 3 suggests that, generally, the 1-hour and 8-hour concentrations are well correlated spatially, and that major changes in the monitoring network are not needed. However, there are subtle factors that need to be considered to monitor 8-hour ozone concentrations, including:

- Downwind monitoring sites which receive dispersed, transported ozone plumes are more prone to 8-hour exceedances than 1-hour exceedances. This is particularly true for areas without afternoon rush hours which provide fresh NO emissions to titrate the transported ozone. However, these areas tend to be less populated.
- The increased stringency of a threshold such as 0.08 ppm 8-hour (in comparison to 0.12 ppm 1-hour) may require monitoring further downwind of metropolitan areas than is currently done.

Several methods are available to analyze where to site 8-hour ozone monitors; these were described in Section 3, and include the following:

- · Calculate, tabulate, and graphically display the number of exceedances for 1-hour and 8-hour thresholds.
- · Compare locations of the 1-hour and 8-hour exceedances.
- · Prepare and compare diurnal ozone profiles.
- Evaluate the potential for farther downwind sites to exceed the 8-hour standards.
- Evaluate the potential for NO titration to influence ozone concentrations.
- Examine the correlation between the 1-hour and 8-hour standards.

Fig 5-7

¹The terminology in **Figure 5-7**, #3/#1, indicates that a site can be used both as a maximum downwind ozone site as well as an upwind site depending upon the time of day/wind direction.

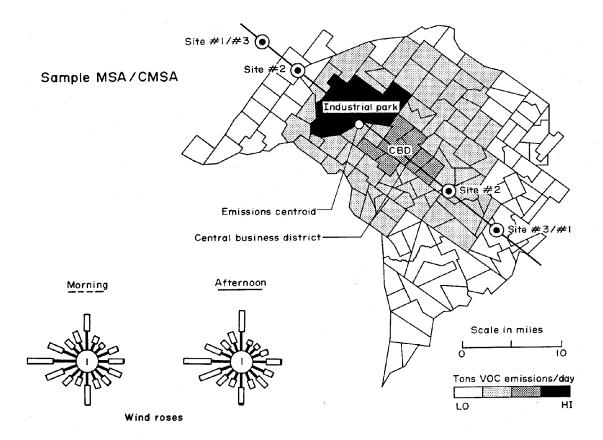


Figure 5-7. Example network design for a metropolitan area with no predominant wind direction (Chu, 1995)

6. MICROSCALE CONSIDERATIONS FOR MONITOR SITING

6.1 GUIDANCE FOR MONITOR PLACEMENT

The previous section provided guidance on determining the general location in a metropolitan area for siting photochemical pollutant monitors. Once the general location is selected, care must be given to selecting a specific location. The site should be selected so that it is in an area of small concentration gradients (i.e., the concentrations measured by the monitor are not affected by small changes in the location of the station). This criterion will be met if the site is located such that no single source contributes disproportionately to the concentrations that are measured, but rather that the measured concentrations reflect the contributions of numerous sources in the area. This section provides criteria for selecting station locations that are representative of the larger area around the station by avoiding large influences of nearby sources and sinks. These recommendations reflect those found in 40 *Code of Federal Regulations* (CFR), Part 58, Appendix E (Probe Siting Criteria for Ambient Air Quality Monitoring).

6.1.1 Vertical and Horizontal Probe Placement

Human exposure is a principal concern associated with high ozone concentrations. The monitor's ozone inlet probe should be placed at a height and location that best approximates where people are usually located. However, due to complicating factors such as obstructions and adsorbing surfaces, probes sometimes need to be more elevated. Considering these issues, probe inlets should be located 3 to 15 meters above ground level. The probe must also be located more than 1 meter vertically and horizontally away from any supporting structure.

6.1.2 Effects of Obstructions

The effects of obstructions such as buildings, trees, and nearby surfaces are important considerations when siting monitors for ozone and nitric oxide because of the effect obstructions have on airflow and pollutant mixing, and the destruction of these species upon contact with some surfaces. Therefore, it is important that sampling be done at a location where the air has had as little contact as possible with nearby surfaces. **Figure 6-1** shows a schematic representation of airflow around a sharp-edged building based on the work of Halitsky (1961) and Briggs (1973). This figure shows that air in the "cavity zone" (the region beyond the building where the airflow is influenced by the obstruction of the building) will make considerable contact with the building. Conversely, air outside the cavity zone will have passed over the building with minimal contact. According to Briggs (1973), the cavity zone extends to roughly 1.5 building heights downwind of the building. Using this as a guide, the minimal allowable distance separating samplers and obstructions should be at least twice the height of the obstruction protrudes above the inlet. **Figure 6-1** also illustrates why it is recommended that inlets along the side of a building be avoided. There is airflow up the side of the building which has considerable contact with the building and allows a substantial possibility for deposition of the pollutant on the surface.

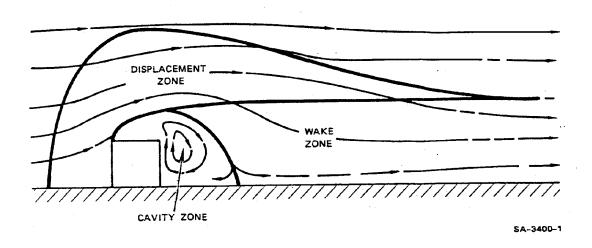


Figure 6-1. Schematic representation of the airflow around an obstacle such as a building [EPA, 1978, based on the work of Halitsky (1961) and Briggs (1973)].

The inlet for sampling must extend above the roof of the building to avoid the complicated airflow within the cavity zone. If the building which houses the instrument is small (i.e., less than 2 meters high), then an extension of the inlet above the roof by a distance of about 1.5 meters should be sufficient (1 meter minimum). For taller buildings it may not be possible to avoid the cavity zone on top of the building without using an inlet line that is so long that it will introduce pollutant losses of its own. If sampling from the top of a tall building is unavoidable, then it is recommended that the inlet be placed toward the upwind side of the building. Airflow must be unrestricted in a horizontal arc of at least 270 degrees around the inlet probe, and the predominant wind direction for the season of greatest pollutant concentration potential must be included in the 270 degree arc. If the probe is located on the side of a building, a 180-degree clearance is required.

6.1.3 Separation from Roadways

For oxides of nitrogen, most fresh combustion emissions are in the form of NO, which rapidly reacts with ozone to form NO₂ resulting in a decrease in ozone concentrations. U.S. EPA (1978) included a kinetic model to predict the change in the ozone concentration for incremental additions of NO_x. Using this model, it was possible to estimate the proper distance from a roadway for placement of an ozone monitor so that the ozone concentration is not depressed to a level where the concentration measurement is not representative of the surrounding area. The EPA has updated this analysis, and the results are shown in **Table 6-1**. This table provides the minimum separation distance between roadways and ozone monitors based on the vehicle traffic of the road.

6.1.4 Spacing from trees and other vegetation

Ozone is known to deposit on trees and other vegetation, thereby reducing the ambient ozone concentration in that area. Additionally, large trees or stands of trees can obstruct normal wind flow patterns. To minimize the effects of individual trees on measured ozone concentrations, inlet probes should be placed at least 20 meters from the "drip line" of trees (the area around the tree where water dripping from the tree may fall). Given that ozone deposition on some trees is very significant, it is further recommended that the sampler be at least 10 meters from the drip line of trees that are located between the urban city core areas and the sampler along the predominant summer daytime wind direction. If the tree is very significant in size, or there is a stand of trees, these should be treated as a building (see guidance above).

6.2 USE OF SATURATION MONITORING

Following the use of the sector analysis described in Section 5. for locating a suitable area for a monitor, one approach for finding a specific location is to develop a short-term sampling study. In this type of study, numerous portable monitors are employed during a period of high ozone concentration at various candidate sites within the sectors identified by the meteorological analysis as having the potential for maximum ozone concentrations. Analysis of data over the period of about a month could be used to determine the best monitor location.

Table 6-1. Separation distance between ozone monitors and roadways (i.e., the minimum distance between the edge of the nearest traffic lane and the monitor).

	Minimum Separation
Roadway Average Daily	Distance Between Roadways
Traffic Vehicles Per Day	and Stations (meters) ^a
<10,000	>10
15,000	20
20,000	30
40,000	50
70,000	100
>110,000	>250

^a Distances should be interpolated based on traffic flow.

Source: 40 CFR Part 58, Appendix E, "Probe siting criteria for ambient air quality monitoring."

This technique was successfully applied during the Wasatch Front Ozone Saturation Study (Start et al., 1994). The State of Utah was required to install two new monitoring sites in the Wasatch Front and conducted this study to determine the optimal location of these monitoring sites. The study was also useful for assessing whether the existing ozone monitoring sites were properly located. The study employed Ogawa passive samplers (Koutrakis et al., 1993), which are small, inexpensive diffusion samplers (i.e., no pump is required) that are useful for obtaining integrated average ozone concentrations over a sampling period, usually on the order of 12-24 hours. The study made measurements at 62 passive sampler locations, and also placed passive samplers at each of the current ozone monitoring sites. The locations of the sites are shown in **Figure 6-2**. Sampling occurred over a 30-day period. However, sampling only occurred on 7 of the 30 days which were expected to have elevated ozone concentrations. Each sampler was exposed for 24 hours to give a one-day integrated sample. The passive samplers performed well, and the study provided an inexpensive means of better understanding the spatial distribution of ozone in the Wasatch Front.

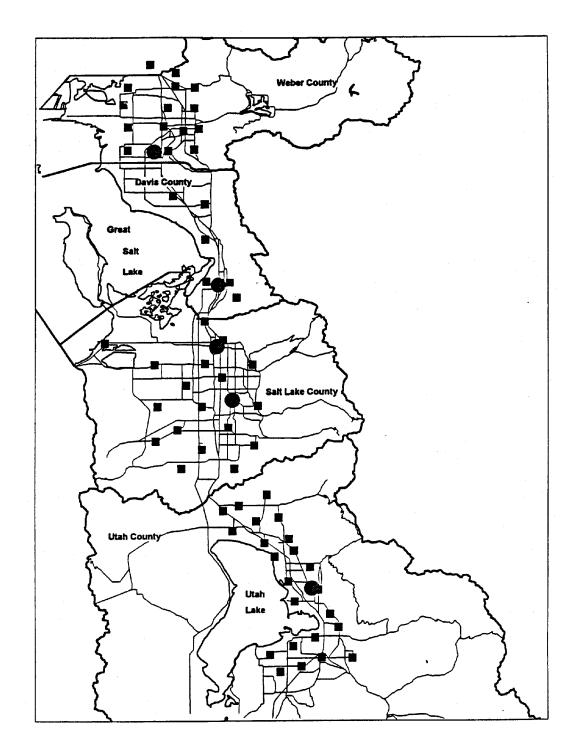


Figure 6-2. Monitor locations for the Wasatch Front Ozone Satuation Study summer 1993 (Start, 1994)

7. RECOMMENDATIONS

As a primer on ozone monitoring issues, this report has touched on a number of key issues and their implications for monitoring network design including: ozone's formation and spatial distribution; monitoring objectives, such as regulatory compliance and scientific research; big picture geographic issues, such as the need for siting monitors upwind of an urban area; and micro-scale issues, such as the need to avoid siting monitors too close to trees and buildings. Readers with an interest in either developing a new ozone monitoring network, assessing the efficacy of an existing network, or updating an existing network to monitor 8-hour ozone concentrations should all find this report's contents to be of value. In summarizing the report the focus has been to organize information in a way that answers commonly asked questions. As has been mentioned throughout the text, the reader is referred to the Appendices for more detailed information concerning the science behind ozone formation, as well as the many additional resources available to assist in designing and implementing monitoring networks. Each of the question and answer discussions in this section concludes with a reference to the earlier report chapters that provides additional relevant information.

How many monitors are enough to provide adequate coverage for a particular region?

The EPA has established minimum network regulatory requirements on how many NAMS and PAMS monitors are required. The EPA guidelines serve as minimum requirements beyond which additional monitoring through the SLAMS network provides better documentation of air quality in a community.

EPA requirements vary depending upon the population and nonattainment status of a particular area. For all urbanized areas with more than 200,000 people, two NAMS sites are required, the maximum downwind site and the maximum exposure site. In addition, EPA requires PAMS VOC, ozone, and nitrogen dioxide monitoring for serious, severe, and extreme ozone nonattainment areas. Areas with less than 500,000 people are required to have at least two PAMS sites, areas with 500,000 to 1,000,000 people are required to have at least three sites, areas with 1,000,000 to 2,000,000 people need four sites, and areas with more than 2,000,000 people need at least five PAMS sites (U.S. EPA, 1994). Appendix B to this document includes references for more PAMS related information.

Scientifically, the number of monitors needed is a function of the region's size and topographic and meteorological complexity. At a minimum, two monitors can be sufficient for a relatively small metropolitan area. EPA recommends that a region using only two monitors site these as (1) a downwind site to measure peak ozone concentrations in a populated area and (2) a site to measure maximum population exposure. A relatively low-cost enhancement would be a monitor at a third location designed to measure upwind, or background, ozone concentrations. Examples of when additional monitors would be necessary include:

Additional monitors will be needed if the region's high ozone concentration days are triggered by any
one of several different meteorological scenarios. When prevailing winds differ depending upon the
high-ozone meteorological scenario, additional monitors are needed to evaluate each scenario's upwind
and downwind locations.

 Multiple monitors will be needed if an area is quite large geographically, with multiple communities in downwind locations. Multiple downwind monitors will be needed to adequately measure peak ozone in the affected areas.

Additional monitors would also be necessary to measure concentrations in an urban core; to address special studies focused on particular areas; to monitor areas with complex terrain; to monitor the effects of specific sources; and to quality assure the existing monitoring network from time to time by collocating monitors near existing monitors, or by conducting saturation monitoring to ensure that the highest upwind and downwind concentrations are being measured.

[Refer to Section 4 of the report for more detailed information.]

How should monitors be sited to properly account for wind direction?

Some straightforward meteorological evaluations can help determine how to site monitors to properly account for prevailing winds. Wind roses need to be constructed for the metropolitan area to identify what direction the wind originates from at given times of day, as well as the wind strength during these time periods. Note that the wind strength is important to help determine how quickly pollutants will travel downwind and be dispersed. Some general "rules of thumb" can assist in this evaluation:

- · Identify days when high ozone concentrations are known to occur. If these days are not yet known, identify days when high ozone concentrations are likely to occur. Methodologies are available to help with this analysis, which utilize wind, temperature, and relative humidity data (Cox, 1995).
- · Construct wind roses for morning (7:00-10:00 a.m.) and afternoon (1:00-4:00 p.m.) winds for high ozone days. Morning wind direction can help determine where to site upwind monitors; afternoon wind direction can help determine where to site downwind monitors.

Note that it is important to distinguish between average summer days, and days when high ozone concentrations are likely to occur. Prevailing average winds may be different than winds on high ozone days. Also note it is possible that more than one meteorological regime is contributing to high ozone formation.

[Refer to Section 5 of the report for more detailed information.]

How should monitors be sited to avoid problems in the immediate vicinity of the monitor (e.g., from roads, trees, buildings)?

Large obstructions, such as tall buildings, and small obstructions, such as trees, can each contribute to inaccurate pollutant measurements if monitors are sited too close to the obstruction. "Rules of thumb" to consider include:

• Generally, monitoring probe inlets should be located 3 to 15 meters above ground, and at least 1 meter vertically and horizontally away from the supporting structure.

- The downwind sides of large obstructions such as buildings or stands of trees include wind pockets that are not representative of the surrounding air mass. Multiplying the height of the obstruction by 10 yields a distance equal to the desired distance between the base of the obstruction and the monitor. If space of that magnitude is not available, the minimal acceptable distance between such obstructions and monitors is 2 times the height of the obstruction. It is important to note, however, that EPA guidance sets a distance goal of 10 times the height of the object.
- Fresh NO emissions titrate ozone. Thus, ozone is quickly reduced in the vicinity of roadways with any significant amount of traffic. Monitors should be placed anywhere from at least 10 to at least 250 meters from a roadway, depending upon the extent of traffic. Existing monitors can be quality assured by analyzing their monitoring data. Frequent measured ozone values in the range of 0 to 30 ppb of ozone may be an indicator that the site is too close to fresh NO emissions. Natural ozone background concentrations are on the order of 40 ppb, prior to pollutant contributions that increase observed concentrations. Measured concentrations in the 0 to 30 ppb range are an indicator of ozone titration and should trigger a review of the monitor site and its proximity to emission sources.

[Refer to Section 6 of the report for more detailed information.]

Are existing 1-hour monitors still useful for 8-hour monitoring, or should they be moved? In particular, does an 8-hour standard mean that the geographic area monitored needs to be enlarged, and if so, by how much?

The locations of existing 1-hour monitors are likely to remain appropriate for monitoring upwind contributions and downwind peak concentrations. There will possibly be a need however, for additional monitors to be located further downwind than those established for 1-hour monitoring. These will help determine the maximum downwind distance where 8-hour exceedances occur.

There is a strong correlation between 0.12 ppm 1-hour and 0.08 ppm 8-hour ozone concentrations, in terms of the general locations of exceedances. There is also a strong correlation between the locations of peak 1-hour and 8-hour ozone concentrations. A key difference between 1-hour and 8-hour ozone concentrations, however, is that downwind of a metropolitan area, 8-hour concentrations tend to exceed the 0.08 threshold more often than 1-hour concentrations exceed the 0.12 ppm threshold. This means that when monitoring 8-hour ozone concentrations, it is probable that the area to be monitored needs to be increased in geographic size in comparison to the area monitored for 1-hour ozone concentrations.

A "rule of thumb" may be as follows: 1-hour peak ozone concentrations are observed approximately 4 to 6 hours downwind of the location of the maximum emissions region (usually the urban core). When monitoring for 8-hour ozone concentrations, however, ozone exceedances may be observed over a broader geographic area than the typical 1-hour exceedance locations. An 8-hour monitoring network would likely benefit by adding monitors to the existing 1-hour network. One suggestion might be to place the additional monitors approximately 1 to 2 hours further downwind from where monitors are normally sited to measure peak 1-hour concentrations. Consideration of the location for the monitor for the potentially affected population must be balanced with the need to capture maximum downwind concentrations outside populated areas.

[Refer to Sections 3 and 5 of the report for more detailed information.]

How can monitor sites be quality assured to determine if they are located in appropriate downwind locations to identify peak ozone concentrations?

The only practical way to assure whether downwind monitors are observing peak ozone concentrations is to locate additional monitors further upwind and downwind to see whether measured ozone concentrations are higher or lower than the existing monitor. Another possibility is to conduct photochemical air quality computer modeling to predict the location of peak ozone concentrations, and to compare the modeling results to the existing or planned network (EPA has issued separate guidance with detailed computer modeling guidelines). An important consideration is how long ago the existing monitoring network was established. If the monitors were sited many years ago, and the area has since undergone significant growth, peak ozone concentrations may be migrating further downwind in the direction of the growth. Additionally, special studies, such as those described in Section 6.2 of this document, can be used as an adjunct to network/site evaluation.

[Refer to Section 3 of the report for more detailed information.]

Should 8-hour ozone monitoring be conducted during the same time of the year as 1-hour ozone monitoring?

The EPA has established ozone seasons for the 1-hour standard which are published in the Code of Federal Regulations (40 CFR 58, Appendix D). However, given differences in the spatial distribution of 1-hour and 8-hour exceedances, and because the 8-hour standard is stricter than the 1-hour standard, adjustments to these seasons may be necessary. The EPA is recommending (EPA, 1998) initial 8-hour ozone seasons for each state to be defined as the period of time beginning with the first month with any daily 8-hour concentration greater to or equal to a 0.080 ppm threshold, and ending with the last month with such exceedances. Adjustments to these initial ozone seasons are expected to better reflect the need for similar ozone monitoring seasons within ozone transport areas; and to consider states with large geographic areas without available ozone data.

[Refer to Section 4 of the report for more detailed information.]

How should monitor siting differ depending upon whether an area is an isolated urban area, is part of an urban corridor which includes numerous metropolitan areas, or is an urban area with multiple prevailing wind directions?

Answering this question helps summarize a number of the issues presented in this report. The information presented here draws upon the real world examples provided by the San Francisco Bay Area's monitoring network. The San Francisco Bay Area offers a good example of a reasonably complex area with monitors in a variety of locations that serve multiple needs. Among the San Francisco Bay Area's numerous monitoring locations are several major metropolitan areas: San Francisco itself, San Jose to the south and east of San Francisco, Oakland to the east, and a number of less populous areas to the north, east, and south (**Figure 3-1** illustrates the geographic relationship among Bay Area cities). In addition, Sacramento is approximately 90 miles to the northeast of San Francisco, and the proximity between the two regions helps to illustrate the value of monitoring sites located between neighbor regions. This

section concludes with five different monitoring scenario discussions that utilize the San Francisco Bay Area as a real world example.

- San Jose: an urban area influenced by pollutant transport. San Jose experiences pollutant transport from its upwind neighbors in the Bay Area, and contributes pollutants to downwind sites. Prevailing winds influencing San Jose's ozone concentrations are generally from the northwest. Therefore, useful monitor locations include San Jose itself, upwind locations to the northwest, and downwind locations to the southeast. Bay Area cities within this geographic sphere include Oakland, San Leandro, Hayward and Fremont to the northwest, and Gilroy to the southeast, all of which have monitors. San Jose is one of the areas where peak ozone concentrations are observed in the San Francisco Bay Area. The Gilroy monitor to the southeast of San Jose both monitors the effects of downwind transport from San Jose on the Gilroy area and serves to confirm that ozone concentrations monitored in San Jose are higher and, therefore, representative of peak concentrations. The monitors stretching to the northwest of San Jose provide a range of upwind ozone concentration measurements that enable San Jose to track the transport of ozone and ozone precursors into its metropolitan area.
- San Francisco: an urban area influenced by clean upwind air conditions. Metropolitan areas that are generally located downwind from and near other metropolitan areas should expect to receive and be influenced by pollutant transport unless one of two conditions occur: (1) extremely fast-rising mixing heights occur which enable ozone concentrations to mix and become dispersed aloft or (2) strong afternoon winds with clean air sweep through the region and remove locally generated and transported pollutants. San Francisco is a coastal city with the Pacific ocean to its west. Afternoon winds tend to be strong due to the sea breeze, and are relatively clean coming from the Pacific ocean. In contrast to its neighbor city, San Jose, San Francisco is relatively free from the influence of pollutant transport, and thus has little need for upwind monitoring.
- Bethel Island: a downwind area that exceeds the 8-hour but not the 1-hour ozone thresholds. The San Francisco Bay Area's peak 1-hour and 8-hour ozone concentrations occur in the same general areas: to the east and to the south of the Bay Area. However, there are areas in the far downwind portions of the Bay Area that exceed a 0.08 ppm 8-hour ozone threshold without exceeding the 0.12 ppm 1-hour threshold. Bethel Island, east of the Bay Area, is an example site exceeding the 8-hour, but not the 1-hour threshold. Bethel Island receives transported ozone and ozone precursors late in the day that contribute to higher late afternoon ozone concentrations. These peak concentrations are on the order of 120 ppb ozone, but are not quite high enough to exceed the 1-hour 125 ppb threshold. However, when added to the locally generated ozone formed earlier in the day, this transported pollution creates an 8-hour concentration that exceeds the 8-hour threshold.
- The greater San Francisco Bay Area: an area with several predominant wind directions contributing to high ozone concentrations. The greater San Francisco Bay Area experiences high ozone concentrations to the northeast, the east, and the southeast of downtown San Francisco. These coincide with the varying meteorological regimes that contribute to ozone formation in the Bay Area, as well as the region's topographic complexity, which includes two mountain ranges that run northwest to southeast (to the south and east of the Bay Area); a river channel that heads to the northeast; a southeastern basin surrounded by San Francisco Bay to the north; and the two mountain ranges that sweep toward one another at the Bay Area's southern rim. To accommodate these meteorological and topographic conditions, the Bay Area has established ozone monitors in numerous locations. Several are located in a line extending through the region from the southwest to the northeast, to the east, and to the southeast. There are also numerous background monitors located in rural areas to the north. By arranging monitors

in this manner, the Bay Area is able to measure ozone concentrations along the predominant wind directions that occur during conditions favorable to ozone formation. The large number of monitors enables the Bay Area to measure peak concentrations with relative confidence, since the area also measures downwind concentrations which are less than peak concentrations.

San Francisco to Sacramento: metropolitan areas with neighboring monitoring networks. When two metropolitan areas are located in close proximity to one another, their monitoring networks provide an opportunity to measure pollutant concentrations relevant to each other's area. The San Francisco and Sacramento, California areas provide an example of this situation. Under some conditions, pollutants are transported to the northeast of San Francisco as far as the Sacramento metropolitan area, some 90 miles away. The San Francisco to Sacramento corridor is an area of continued growth, and several monitoring sites are located along the northeast path that connects the two cities. Monitors located in between these metropolitan areas can serve a dual purpose: for example, monitors to the southwest of Sacramento may have been sited to provide background or upwind readings for the Sacramento area. Depending upon the meteorological conditions present, these same monitors may also serve to provide downwind ozone concentrations for the San Francisco Bay Area. Note that in areas where pollutant transport is a significant ongoing event, such as in the northeastern U.S. ozone transport region (OTR), monitors between major urban areas may record more uniform pollutant concentrations in comparison to the San Francisco example cited here. In those cases, the appropriate location of downwind monitors will be a function of (1) downwind ozone concentrations and (2) proximity to neighbor metropolitan areas.

[Refer to Section 3 of the report for more information and maps of the areas discussed.]

8. REFERENCES

- Altshuller A.P. and Lefohn A.S. (1996) "Background ozone in the planetary boundary layer over the United States". *J. Air & Waste Manag. Assoc.* **46**, 134-141.
- Briggs G.A. (1973) *Diffusion Estimation for Small Emissions*. Draft No. 79 in 1973 annual report of the Atmospheric Turbulence and Diffusion Laboratory, Oak Ridge, TN., Report No. ATDL-106, 83-195.
- Carter W.P.L. (1994) "Development of Ozone Reactivity Scales for Volatile Organic Compounds". *J. Air & Waste Manag. Assoc.* **44**, 881-899.
- Chu S.-H. (1995) "Meteorological Considerations in Siting Photochemical Pollutant Monitors". *Atmos. Environ.* **29**, 2905-2913.
- *Code of Federal Regulations* (1997) Title 40, Part 58, Appendix D. "Network Design for SLAMS, NAMS, and PAMS"., published by United States Government.
- Cox W.M. and Chu S.H. (1993) "Meteorologically Adjusted Ozone Trends in Urban Areas: a Probabilistic Approach". *Atmos. Environ.* **27B**, 425-434.
- Halitsky J. (1961) "Estimation of Stack Height Requirements to Limit Contamination of Building Air Intakes". *J. Amer. Ind. Hyg. Assoc.* **26**, 106-115.
- Husar R.B. (1996) *Pattern of 8-hour Daily Maximum Ozone and Comparison with the 1-hour Standard*. Report prepared by the Center for Air Pollution Impact and Trend Analysis for the OTAG Air Analysis Workgroup, posted on the OTAG Air Analysis Web Site, URL='http://capita.wustl.edu/otag/'.
- Koutrakis P., Wolfson J.M., Bunyaviroch A., Froehlich S.E., Hirano K., and Mulik J.D. (1993) "Measurement of Ambient Ozone Using a Nitrite-coated Filter". *Anal. Chem.* **65**, 209-214.
- National Research Council (1991) *Rethinking the Ozone Problem in Urban and Regional Air Pollution*. National Academy of Sciences/National Research Council, National Academy Press, Washington, DC.
- Reiss R., Chinkin L.R., and Main H.H. (1995a) "Ozone NAAQS Review--ambient Air Monitoring Support Target Strategy. Work assignment 1-95. Final report prepared for U.S. Environmental Protection Agency, Research Triangle Park, NC by Sonoma Technology, Inc., Santa Rosa, CA, EPA Contract No. 68D30020, STI-94510-1535-FR, September.

- Reiss R., Chinkin L.R., Roberts P.T., Main H.H., and Eisinger D.S. (1995b) *Investigation of Monitoring Networks for an Alternative Ozone NAAQS*. Work assignment 7-95. Final report prepared for U.S. Environmental Protection Agency, Research Triangle Park, NC by Sonoma Technology, Inc., Santa Rosa, CA, EPA Contract No. 68D30020, STI-94571-1553-FR, December.
- Seinfeld J.H. (1986) *Atmospheric Chemistry and Physics of Air Pollution*. Wiley Interscience, New York, NY, pp. 154-156.
- Start G.E. (1994) *Wasatch Front Ozone Saturation Study Summer 1993*. Report prepared for the State of Utah Department of Environmental Quality by U.S. Department of Commerce, National Oceanic and Atmospheric Administration, Idaho Falls, ID.
- U.S. Environmental Protection Agency,(1978) *Site Selection for the Monitoring of Photochemical Air Pollutants*. Office of Air Quality Planning and Standards, Research Triangle Park, NC, EPA-450/3-78-013, April.
- U.S. Environmental Protection Agency (1989) *Quality Assurance Handbook for Air Pollution Measurement Systems*. Volume IV meteorological measurements. Report prepared by the Office of Research and Development, Atmospheric Research and Exposure Assessment Laboratory, U.S. Environmental Protection Agency, Research Triangle Park, NC, EPA/600/4-90-003.
- U.S. Environmental Protection Agency (1996) Clearinghouse for inventories and emission factors. On U.S. Environmental Protection Agency electronic bulletin board.
- U.S. Environmental Protection Agency (1998) *Guideline for Selecting and Modifying the Ozone Season Based on an 8-Hour Standard*, Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina, EPA-454/R-98-001, April.
- U.S. Environmental Protection Agency (1994) *Photochemical Assessment Monitoring Stations Implementation Manual*, Office of Air Quality Planning and Standards, Research Triangle Park, North Carolina, EPA-454/B-93-051, March.

APPENDIX A

BACKGROUND ON OZONE FORMATION

APPENDIX A: BACKGROUND ON OZONE FORMATION

OVERVIEW

Ozone is formed as a product of photochemical reactions involving several components, the primary contributors being volatile organic compounds (VOC) and oxides of nitrogen (NO_x). This appendix includes a brief discussion of the atmospheric chemistry governing ozone formation. The material in this discussion is based on Seinfeld (1986).

As discussed in the main body of the report, the photolysis of NO_2 in sunlight produces NO and O, and the free oxygen atom rapidly combines with O_2 and forms ozone (O_3) :

$$NO_2 + hv \xrightarrow{k_1} NO + O$$
 (A-1)

$$O + O_2 + M \xrightarrow{k2} O_3 + M \tag{A-2}$$

where hv represents photochemical energy from ultraviolet radiation (or a photon), k_1 and k_2 represent rate constants for the reaction of NO_2 and hv, and M represents N_2 , O_2 or another molecule that absorbs the reaction's excess vibrational energy. Once formed, ozone is rapidly dissociated by reaction with NO, as follows:

$$O_3 + NO \xrightarrow{k1} NO_2 + O_2 \tag{A-3}$$

The NO₂ molecule is regenerated, and in the absence of other species a steady state is achieved through reactions (A-1) through (A-3) in which the ozone concentration can be estimated by the following relationship:

$$[O_3] = \frac{k_1[NO_2]}{k_3[NO]}$$
 (A-4)

where k_1 and k_3 are the rate constants for reactions (A-1) and (A-3).

Ozone in the clean troposphere is governed almost solely by the relationship described by reaction (A-4). In the more polluted troposphere, oxidation of VOC by free radicals have significant effects on ozone formation by converting NO to NO₂. The key to this oxidation process is the OH radical (a radical is a highly reactive molecule) which is formed by ozone photolysis and other reactions. Its reaction with many VOC leads to the formation of peroxyalkyl radicals, as follows:

$$RH + OH \rightarrow R + H_2O$$
 (A-5)

Where RH is a general symbol for a hydrocarbon (which in this context is synonymous with a VOC); $OH \cdot$ is a hydroxy radical (the dot following the OH symbolizes a free electron, which defines a radical); and, $R \cdot$ is the RH molecule without the H (it is thus a free radical hydrocarbon). In the presence of oxygen, the next step in this process is:

$$R \cdot + O_2 \rightarrow RO_2 \cdot$$
 (A-6)

where RO_2 is a free radical oxidized hydrocarbon (a peroxy radical).

Similarly, OH radicals react with aldehydes (<code>RCHO</code>) to form acyl (<code>RCO</code> \cdot) and acylperoxy [<code>RC(O)O2</code> \cdot] radicals.

The peroxy radicals react rapidly with NO to form NO₂ and other free radicals, as follows:

$$RO_2 \cdot + NO \rightarrow NO_2 + RO \cdot \rightarrow RONO_2$$
 (A-7)

$$RC(O)O_2 \cdot + NO \rightarrow NO_2 + RC(O)O \cdot$$
 (A-8)

The [$RC(O)O_2$ ·] radicals normally decompose to alkyl radicals which leads to the generation of another peroxyalkyl radical. This peroxyalkyl radical can oxidize additional NO to NO₂.

Typically, smaller alkoxy radicals react with $\rm O_2$ to form $\rm HO_2$ radicals and a carbonyl compound, as follows:

$$RO \cdot + O_2 \rightarrow HO_2 \cdot + R'CHO$$
 (A-9)

where R'CHO is an aldehyde or carbonyl, R is a general term for a carbon chain, and R' is a different carbon chain. Like other peroxy radicals, the hydroperoxy radical (HO_2) can oxidize NO to NO_2 as follows:

$$HO_2 \cdot + NO \rightarrow NO_2 + OH \cdot$$
 (A-10)

Note that the OH radical is regenerated in this reaction, which completes the cycle. Therefore, this $OH \cdot radical$ is available to react with other VOC species and continue the chain of reactions.

ORGANIC REACTIVITY

As the reactions in the last section show, the mechanism of oxidation of NO to NO_2 by free radicals generated by organic reactions in dependent on the organic species. Both the quantities and type of organic species in the atmosphe re influence formation of ozone. Seinfeld (1986) has identified four factors which influence the efficacy of an organic compound in forming NO_2 molecules, as follows:

- The rate at which the organic compound reacts in the atmosphere (kinetic reactivity) influences how fast the organic converts NO to NO₂ and thud how quickly it causes ozone formation. The most important reaction is with the OH radical.
- The types of product species formed in an organic species reaction with OH (mechanistic reactivity) also influence ozone production rates. The number of molecules of NO which are oxidized per molecule of organic determines how much O₃ will be formed by the consumption of a given amount of the organic. For most compounds, two or three ozone molecules can be formed., However, other compounds can form significantly more molecules.
- As discussed above, the reaction cycle starts with the OH radical. Organic compounds, such as aldehydes and aromatics, where atmospheric reactions result in increased radical levels, increase ozone formation for all other organic compounds. Conversely, organic compounds, such as C5+ alkanes, which depress OH radical concentrations, decrease ozone formation for all other organic compounds.
- Ozone formation can only occur as long as NO_x is present. Thus, organics whose atmospheric oxidation involves significant NO_x sinks will necessarily allow less O₃ formation under conditions when NO_x is limited.

Given the complicated nature of assessing the impact of a particular VOC compound on ozone formation, several scales have been developed. The most widely used is the maximum incremental reactivity scale (MIR) (Carter, 1994). The MIR for a particular VOC compound is determined by adding a small amount of the compound to a typical atmospheric mix where the NO_x has been adjusted to have the strongest ozone inhibiting effect. The MIR is determined by the amount of ozone that is formed after the VOC addition. **Table A-1** summarizes the MIR for several VOC compounds found in the atmosphere. Generally, the olefins and xylenes are the most reactive, while paraffin compounds are the least reactive. It is also worth noting that isoprene, which is the principal biogenic VOC species, has a high reactivity. This scale along with the atmospheric concentration of the compounds can be used to assess the efficacy of reducing a particular VOC compound. The Photochemical Assessment Monitoring Stations (PAMS) network is devoted to quantifying the atmospheric concentrations of these species (Appendix B includes references for further PAMS information).

Table A-1. Maximum incremental reactivity values for hydrocarbon and carbonyl compounds.

Page 1 of 3

		Maximum Incremental Reactivity (MIR) ^a	
Species Name	AIRS No.	g Ozone/ g C	mol Ozone/ mol C ^b
1,3,5-trimethylbenzene	45207	10.1	2.81
t-2-Butene	43216	10	2.92
c-2-Butene	43217	10	2.92
Propene	43205	9.4	2.75
Isoprene	43243	9.1	2.58
1-Butene	43280	8.9	2.6
1,2,3-trimethylbenzene	45225	8.9	2.6
t-2-pentene	43226	8.8	2.57
c-2-pentene	43227	8.8	2.57
1,2,4-trimethylbenzene	45208	8.8	2.45
Cyclopentene	43283	7.7	2.19
Ethene	43203	7.4	2.16
m&p-Xylenes	45109	7.4 ^c	2.05
Formaldehyde	43502	7.2	4.5
t-2-hexene	43289	6.7	1.96
c-2-hexene	43290	6.7	1.96
o-Xylene	45204	6.5	1.8
2-methyl-2-butene	43228	6.4	1.87
3-methyl-1-butene	43282	6.2	1.81
1-Pentene	43224	6.2	1.81
Acetaldehyde	43503	5.5	2.52
Methylcyclopentane	43262	2.8	0.82
Toluene	45202	2.7	0.74
Ethylbenzene	45203	2.7	0.75
Cyclopentane	43242	2.4	0.7

Table A-1. Maximum incremental reactivity values for hydrocarbon and carbonyl compounds.

Page 2 of 3

		Maximum Incremental Reactivity (MIR) ^a	
Species Name	AIRS No.	g Ozone/ g C	mol Ozone/ mol C ^b
styrene	45220	2.2	0.60
Isopropylbenzene	45210	2.2	0.6
n-Propylbenzene	45209	2.1	0.58
Methylcyclohexane	43261	1.8	0.53
2,3,4-trimethylpentane	43252	1.6	0.48
2,4-dimethylpentane	43247	1.5	0.45
3-methylpentane	43230	1.5	0.45
2-methylpentane	43285	1.5	0.45
3-methylhexane	43249	1.4	0.42
i-Pentane	43221	1.38	0.41
2,3-dimethylpentane	43291	1.31	0.39
Cyclohexane	43248	1.28	0.37
i-Butane	43214	1.21	0.37
2-methylhexane	43263	1.08	0.32
2,3-dimethylbutane	43284	1.07	0.32
n-Pentane	43220	1.04	0.31
n-Butane	43212	1.02	0.31
3-methylheptane	43253	0.99	0.29
n-hexane	43231	0.98	0.29
2-methylheptane	43960	0.96	0.29
2,2,4-trimethylpentane	43250	0.93	0.28
2,2-dimethylbutane	43244	0.82	0.25
n-Heptane	43232	0.81	0.24
n-Octane	43233	0.6	0.18
Acetone	43551	0.56	0.23

Table A-1. Maximum incremental reactivity values for hydrocarbon and carbonyl compounds.

Page 3 of 3

		Maximum Incremental Reactivity (MIR) ^a	
Species Name	AIRS No.	g Ozone/ g C	mol Ozone/ mol C⁵
n-nonane	43235	0.54	0.16
Acetylene	43206	0.5	0.14
Propane	43204	0.48	0.15
n-Decane	43238	0.46	0.17
Benzene	45201	0.42	0.11
n-Undecane	43954	0.42	0.12
Ethane	43202	0.25	0.08
Carbon Monoxide	42101	0.054	0.032
Methane	43201	0.015	0.005

Note: compounds are ordered listing those with greatest ozone forming potential first.

Carter (1994). Note that the paper provides only units of g Ozone per
$$\frac{gO_3}{gC} x \frac{1}{MWo_3} x \frac{MWvoc}{\#Cvoc}$$
b Calculated from g Ozone/g C values: where

 MWo_3 = molecular weight of Ozone (48 g/mol), MW_{voc} = molecular weight of the VOC, and # C_{voc} is the number of carbons in the VOC.

 $^{^{\}rm a}$ Carter (1994). Note that the paper provides only units of g Ozone per g C.

^c Average of m-xylene and p-xylene values.

APPENDIX B

SUPPLEMENTAL REFERENCE MATERIALS

APPENDIX B: SUPPL/EMENTAL REFERENCE MATERIALS

On-line Resources

The U.S. EPA operates a world wide web site with a variety of useful information. The Internet address is 'www.epa.gov'. The Office of Air Quality Planning and Standards (OAQPS) has a sub-directory on the site at 'www.epa.gov/oar/oaqps'.

EPA Quality Assurance Guidelines

- 1. "Quality Assurance Handbook for Air Pollution Measurement Systems, Volume I: A Field Guide to Environmental Quality Assurance" U.S. EPA, EPA-600/R-94-038a, April 1994 (or later revision).
- 2. "Quality Assurance Handbook for Air Pollution Measurement Systems, Volume II: Ambient Air Specific Methods" U.S. EPA, EPA-600/R-94-038b, April 1994 (or later revision due out Spring 98).
- 3. "Quality Assurance Handbook for Air Pollution Measurement Systems, Volume IV: Meteorological Measurements" U.S. EPA, EPA/600/4-90/003, August 1989

These 3 quality assurance documents are available through the EPA's Center for Environmental Research Information, 26 W. Martin Luther King Drive, Cincinnati, Ohio 45268, telephone (513) 569-7562, fax (513) 569-7566.

Photochemical Air Monitoring System (PAMS)

"Photochemical Assessment Monitoring Stations Implementation Manual" U.S. EPA, EPA-454/B-93-051, March 1994

This reference document is available through the National Technical Information Service (NTIS), 5285 Port Royal Road, Springfield, VA 22161, telephone (703) 487-4650, fax (703) 321-8547. The PAMS NTIS document number is PB 941 873 82.

Meteorological Data

National Climatic Data Center (NCDC), Asheville, North Carolina, (704) 271-4476. NCDC stores a wide variety of meteorological data from the United States, which can be used for analysis.

EPA Technology Transfer Network (TTN) contains a program to construct wind rose plots. The program can be found within the directory for the Support Center for Regulatory Air Models (SCRAM). The TTN electronic bulletin board can be reached at (919) 541-5742.

The National Weather Service (NWS) operates regional climate centers, which can provide meteorological data. The regional centers include:

- 1.) High Plains Climate Center L.W. Chase Hall University of Nebraska Lincoln, NE 68583-0728 (402) 472-6706
- 2.) Midwestern Climate Center Illinois State Water Survey 2205 Griffith Drive Champaign, IL 61820-7495 (217) 244-8226
- 3.) Northeast Regional Climate Center 1123 Bradfield Hall Cornell University Ithaca, NY 14853 (607) 255-1751
- 4.) Southeast Regional Climate Center 1201 Main Street Suite 1100 Columbia, SC 29201 (803) 765-0849
- 5.) Southern Regional Climate Center 245 Howe-Russell Complex Louisiana State University Baton Rouge, LA 70803 (504) 388-5021
- 6.) Western Regional Climate Center
 Desert Research Institute
 P.O. Box 60220
 Reno, NV 89506-0220
 (702) 677-3106

Code of Federal Regulations

The following citations include specific monitoring requirements as outlined in the Code of Federal Regulations.

40 CFR Part 58, Appendix D - Network Design for State and Local Air Monitoring Stations (SLAMS), National Air Monitoring Stations (NAMS), and Photochemical Assessment Monitoring Stations (PAMS).

40 CFR Part 58, Appendix E - Probe Siting Criteria for Ambient Air Quality.